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PLANT BIOMARKERS AS A PROXY TO STUDY HIGHLY DECOMPOSED FEN PEAT

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ACADEMIC DISSERTATION

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ABSTRACT

Northern peatlands form a large storage of terrestrial carbon and at the same time they provide an important palaeoecological archive to study past climate changes and associated carbon dynamics. One of the most widely used methods to study peatland histories is the plant macrofossil method. However, peat material of the early succession stages, the fens, is often highly decomposed hampering the identification of the fossil plant remains. Thus, current methods may give only a partial view on the past vegetation, and as a result the accuracy of carbon balance estimations and climate implications may remain low. A new promising method to study past plant assemblages from peat is the geochemical plant biomarker method, which has performed well in less decomposed bog peat environments.

In my study I assess the applicability of the geochemical plant biomarker method to study past plant assemblages from highly decomposed fen peat. For the first time I apply a living fen plant biomarker training set to study past fen phases. To do this, I collected and analysed two sets of living key fen plants. The training sets included boreal fen, arctic fen and permafrost peat plateau plants. The biomarker analyses on fossil peat were applied in parallel with macrofossil analyses to two boreal and one arctic permafrost peat section, all known to contain highly decomposed peat.

The analyses of living plants showed that the biomarker compositions did not differ between the same species collected from different bioclimatic zones, suggesting that, at least to some extent, plant biomarkers can be used universally beyond the geographical areas where the training set was collected. The plant biomarker analyses indicate that the *n*-alkanes, and their ratios, are the most useful compounds to separate fen plant groups: *Sphagnum* mosses and vascular plants. Results showed also that biomarker composition of fen plants did not differ substantially from their bog counterparts. However, results indicated that when a wider combination of plants, plant parts and peatland habitats are incorporated into the training set the data interpretation becomes more challenging. For example, the biomarker composition of *Sphagnum* mosses and sedge roots resembled each other despite their differences in biology. Thus, a larger set of proxies is advisable when plant groups need to be separated more accurately.

In the peat sections studied here, the biomarker method performed well in less humified bog peat layers but less well in the highly decomposed fen peat layers. The macrofossil method proved to be most competitive proxy to reconstruct past vegetation assemblages and local environmental conditions through-out the peat sections. However, when macrofossil and biomarker data were interpreted in parallel, it became clear that biomarkers were also able to reflect the major changes in dominating plant groups and in moisture conditions. Accordingly, the analysis separated the most important bog microhabitats and the major regime shifts from fen to bog. I conclude, however, that in fen environments the interpretation of biomarker data can be rather challenging. As a result, it appears that the biomarker method, as applied here, performs the best as a complimentary proxy when used in conjunction with macrofossils, and that the data should be interpreted cautiously.

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications, referred to in the text by their Roman numerals:

I Ronkainen T., McClymont E. L., Väliranta M. and Tuittila E.-S. (2013). The *n*-alkane and sterol composition of living fen plants as a potential tool for palaeoecological studies. *Organic Geochemistry* 59, 1–9. doi:10.1016/j.orggeochem.2013.03.005

II Ronkainen T., McClymont E. L., Tuittila E.-S. and Väliranta M. (2014). Plant macrofossil and biomarker evidence of fen-bog transition and associated changes in vegetation in two Finnish peatlands. *Holocene* 24, 828-841. doi: 10.1177/0959683614530442

III Ronkainen T., McClymont E. L., Biasi C., Tuittila E.-S., Väliranta M. Salonen, S.S, and Fontana, S. (2014). Combined biogeochemical and paleobotanical approach to study permafrost environments and past dynamics. *Journal of Quaternary Science:* doi:10.1002/jqs.2763.

AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

For all the publications T. Ronkainen prepared and analysed biomarkers and macrofossil samples under the guidance of E. McClymont and M. Väliranta, respectively. T. Ronkainen was responsible for TOC measurements for studies I and II.

I The study was planned by all authors. T. Ronkainen and M. Väliranta, with help from A. Laine, were responsible for collecting the plant samples. T. Ronkainen and E-S. Tuittila analysed the data. T. Ronkainen prepared the manuscript, with contributions from M. Väliranta, E. McClymont and E-S. Tuittila.

II The study was planned by all authors. E-S. Tuittila was responsible for collecting the peat cores. T. Ronkainen and E-S. Tuittila analysed the data. T. Ronkainen prepared the manuscript, with contributions from M. Väliranta, E. McClymont and E-S. Tuittila.

III The study was planned by T. Ronkainen, M. Väliranta and C. Biasi. T. Ronkainen and M. Väliranta collected plant samples. D. Kaverin performed coring. S. Salonen and S. Fontana analysed the pollen samples. S. Salonen produced the age-depth model. T. Ronkainen analysed the data with contribution from E-S. Tuittila. T. Ronkainen was responsible for writing the manuscript with contributions from M. Väliranta, E. McClymont, E-S. Tuittila and C. Biasi.

ABBREVIATIONS

ACL	average chain length [Σ (C_n x n)/Σ (C_n)]
Al_2O_3	aluminium oxide
amu/s	atomic mass unit / second
C	carbon
cal yr BP	calibrated years before present
CPI	carbon preference index [Σ_{odd} ($C_{21} - C_{31}$) + Σ_{odd} ($C_{23} - C_{35}$)/ (2 Σ_{even} ($C_{22} - C_{34}$)]
CH_4	methane
CO_2	carbon dioxide
CH_2Cl_2	dichloromethane
DCA	detrended correspondence analysis (unconstrained (indirect) gradient analysis)
FID	flame ionization detector
GC-MS	gas chromatograph – mass spectrometry
H	nitrogen
He	helium
KOH	potassium hydroxide
M	molar concentration
MeOH	methanol
N	nitrogen
NaOH	sodium hydroxide
N_2	nitrogen
N_2O	nitrous oxide
O	oxygen
P_{aq}	(n-C_{23}+n-C_{25})/(n-C_{23}+n-C_{25}+n-C_{29}+n-C_{31})
PCA	principal component analysis (unconstrained (indirect) gradient analysis)
Pg	1 Pg = 10^5 g
P_{wax}	(n-C_{27}+n-C_{29} +n-C_{31})/(n-C_{23}+ n-C_{25}+ n-C_{27}+ n-C_{29}+ n-C_{31})
RDA	redundancy analysis (constrained (direct) gradient analysis)
S	sulphur
TLE	total lipid extraction
TOC	total organic carbon
UOM	un-identified organic matter
^{14}C	radiocarbon, a radioactive isotope of carbon
Σ	sum
μ	micro; denoting a factor of 10^{-6}

1 INTRODUCTION

Northern peatlands store approximately 30% of the terrestrial carbon (Gorham, 1991). They comprise *c*. 90 % (≈ 4 x 10^6 km^2) of the global peatland area (Yu et al., 2010) containing *c*. 90 % (473-621 Pg) of the total carbon pool stored in the peatlands in form of peat (Loisel et al., 2014; Yu, 2011).

As a consequence, northern peatlands play an important role in atmospheric carbon cycling as carbon sinks yet, simultaneously, they are a natural source of another effective greenhouse gas, CH_4, to the atmosphere (Frolking and Roulet, 2007; Matthews, 2000). Major peatland types, namely bogs and fens, support different vegetation and consequently differ in their carbon (CO_2 and CH_4) dynamics (e.g. Laine et al. 2007; Riutta et al. 2007; Maanavilja et al. 2011). In addition, permafrost peatlands are found to have relatively large N_2O emissions (Repo *et al*., 2009; Marushchak *et al*., 2011), which binds northern peatlands tightly into the global nitrogen cycle as well.

After the early-Holocene (starting *c*. 11 700 years ago) initiation (MacDonald et al., 2006; Yu et al., 2010) northern peatlands have undergone successional changes due to autogenic processes, i.e. rise of the peat surface due peat accumulation, and changes in environment and climate. Information of the past environmental changes is stored in the historical peat layers in the form of partially preserved plant and animal remains. Hence, peatlands form important palaeo-environmental archives spanning over thousands of years.

The speed and rate of climate change in the northern regions are under debate in scientific and political arenas (IPCC, 2013). As carbon dynamics are an essential part of these discussions there is a growing interest to understand functioning and feedback mechanisms of peatlands under changing climate. Therefore there is also a constant demand for new and more accurate methods to reconstruct past changes in peatland dynamics. In my work I explore the applicability of the geochemical plant biomarker method to study peatland histories from highly decomposed fen peat layers, as more traditional methods, such as macrofossil analysis, may potentially provide only a relatively limited amount of information of these important peat layers.

1.1 PEATLAND SUCCESSION – FORMATION OF THE PEAT ARCHIVES

Peat is organic material accumulated over time under excessive moisture conditions. It is mainly composed of dead plant material of various decomposition stages. Peat is a compilation of different plant litter types: wood, leaves, rhizomes and bryophytes, especially *Sphagnum* mosses (Clymo, 1983). Once initiated, southern boreal peatlands especially tend to develop towards stages that are characterized by decreasing base saturation and increasing acidity. This autogenic succession, ombrotrophication, is mainly driven by peat accumulation, which results in changes in the quantity of water and mineral nutrients available to plants living in peatland surface (Rydin and Jeglum, 2006). As a consequence the plant species compositions changes and the peatland undergo a regime shift from nutrient rich fen to nutrient poor bog (Wheeler and Proctor, 2000, Økland et al., 2001).

Figure 1. Fen (left) and bog (right) peatland environments.

During the early succession phase the peatland receives water and nutrients, e.g. nitrogen, phosphorus, and potassium, from precipitation, but also from ground water which is influenced by underlying and surrounding mineral soils. Thus, minerotrophic (nutrient rich) fens sustain nutrient demanding vegetation, such as forbes (e.g. *Menyanthes trifoliata*, *Comarum palustre* syn. *Potentilla palustris*), sedges (e.g. *Carex rostrata, C. nigra, C. livida*), brown mosses (e.g. *Warnstorfia* spp.), and depending on a site, trees (*Picea abies*, *Betula* spp.). The major transition between the two main peatland types, fens and bogs, is often characterized by a

distinct change from *Carex* or *Carex-Sphagnum*-dominated vegetation to *Sphagnum-Eriophorum* sp. or *Sphagnum*-dominated vegetation (e.g. Hughes, 2000; Hughes and Barber, 2003; Tuittila et al., 2013). The ombrotrophication finally leads to the development of a climax bog stage. Bog surfaces are often patterned with microhabitats that sustain different vegetation. Dry hummocks are dominated by *Sphagnum* mosses from Acutifolia section (e.g. *Sp. fuscum*), lichens and dwarf shrubs, while wet hollows are dominated by wet habitat *Sphagna* from Cuspidata section (e.g. *S. cuspidatum, S. majus, S. balticum*) together with sedges (e.g. *Scheuchzeria palustris, Eriophorum* spp.). Lawns represent an intermediate habitat between hummocks and hollows and are often dominated by characteristic lawn species such as *S. magellanicum* (Rydin and Jeglum, 2006).

In addition to the autogenic succession, allogenic factors such as climate, fires, flooding, land uplifting, or changes in catchment water dynamics, can induce or change succession pattern, often over much shorter time-scales (Tuittila et al., 2007). The impact can vary (Tuittila et al., 2013): the allogenic "disturbance" may result in an accelerated or reversed hydroseral succession where e.g. a bog may revert back to a fen stage or a wooded bog revert to open bog (Hughes and Dumayne-Peaty, 2002; Rydin and Jeglum, 2006; McClymont et al., 2008). Any changes in peatland environment may have consequences on the carbon balance of the peatland due the changes in the dominant vegetation (e.g. Riutta et al., 2007; Tuittila et al., 2013).

In conclusion, peatland succession is controlled by autogenic and allogenic factors. Boreal peatlands typically undergo a major regime shift from fen stage to bog stage, which can be detected from historical peat deposits as changes in plant assemblages. The role of climate in past major regime shifts still needs further investigations. Thus, in order to predict future changes in peatland environments it is essential to study the past, to increase our understanding on the climate change driven mechanisms that drive peatland dynamics. Vegetation composition plays an essential role in the ecosystem carbon balance (e.g. Riutta et al., 2007); bryophyte- and vascular plant- dominated communities differ in their CO_2, CH_4 and N dynamics due to plant physiology, microbial activity in peat and prevailing environmental conditions (Laine et al., 2007; Levy et al., 2012; Larmola et al., 2014). Thus it is crucially important to differentiate plant communities as precisely as possible when peatland dynamics are reconstructed back in time (cf. Yu et al., 2013).

1.2 RECONSTRUCTING THE PAST FROM PEAT ARCHIVES

1.2.1 TRADITIONAL PROXIES

Several different biological organisms deposited in peat can be used as proxies to reconstruct different historical information. For example, testate amoebae (a microbial group of protists) are commonly used as a palaeohydrological proxy for estimating the water table depth and moisture conditions (e.g. Charman 1997; Charman et al., 2007). In general, pollen analysis depicts more regional-scale environmental changes (Salonen et al., 2011) even though in case of large peatland massifs pollen assemblages may represent a more local source (e.g. Väliranta et al., 2003). Stable isotopes of carbon and oxygen studied from different peat components can be used to reconstruct past temperatures and precipitation reflecting both the fractionation of isotopes during moisture transport and deposition within the atmosphere, as well as the biological fractionation which can occur under different environmental conditions (e.g. Xie et al., 2000; Kaislahti-Tillman et al., 2013). For reconstructing the past vegetation one of the most useful proxy methods are macroscopic plant remains (e.g. Barber et al., 1998; Mauquoy et al., 2002; Tuittila et al., 2007; Väliranta et al., 2007). The macrofossil method is based on species-level identification of plant remains that in peatland environments represent *in situ* deposition (e.g. Speranza et al., 2000; Mauquoy et al., 2002). When past variations in vegetation are combined to modern ecological knowledge the past plant assemblages can be used to reconstruct various environmental changes: carbon dynamics (e.g. Juutinen et al., 2013, Tuittila et al., 2013), hydrological variations (e.g. Väliranta et al., 2007 and 2012), temperature (e.g. Oksanen et al., 2001) and fire dynamics (e.g. Sillasoo et al., 2011).

In general, the anoxic condition which results from high water table levels leads to a slow and incomplete decomposition process in peat. However, a higher level of decomposition is typical for fen peat due to less recalcitrant litter quality and related higher microbial and enzyme activity, and availability of oxygen as a main driver for decomposition (Bartsch and Moore, 1985; Szumigalski and Bayley, 1996; Freeman et al., 2001;Moore et al., 2007; Strakova et al., 2011). In contrast, the acidity in bogs, created by *Sphagnum* mosses exudates as well as the by-products of the limited bacterial activity, limits the microbial activity which slows down the decomposition rate (Killops and Killops, 2008). As a consequence bog peat often contains plant macrofossils that are fairly easy to identify, while in fen peat layers the plant material is commonly highly decomposed, and this hampers the fossil plant species identification.

1.2.2 BIOGEOCHEMICAL PROXIES - BIOMARKERS

The geochemical biomarker method is based on organic geochemistry, and the fact that carbon is a main constituent of all living organisms on Earth. Carbon is circulated through various biochemical and geochemical transformations ranging from the sedimentary rocks to living systems on the Earth's surface. With several other elements such as H, O, S, and N, carbon atoms form a wide variety of strong organic compounds with high stability and resistance against decomposition. Geochemically the most important basic chemical classes are carbohydrates, proteins and lipids. Higher plants also contain significant amounts of lignin, which is the major component of their supportive tissues (Killops and Killops, 2008).

The biomarker method has been widely used in lacustrine and marine sediments to study the sources of organic matter in sediments, and to generate climate and environmental reconstructions of e.g. sea surface temperatures or historical vegetation (e.g. Cranwell, 1988; Madureira et al., 1997; Schubert and Stein, 1997; Meyers, 2003; Eglinton and Eglinton 2008; Vonk et al., 2008; Castañeda and Schouten 2011; Rosell-Melé et al. 2014). Peatlands are well-suited for biogeochemical biomarker analyses because they store large amounts of organic material, the amount of inorganic material is low, and anoxic conditions favour organic matter preservation (Killops and Killops, 2008). The presumptions made when the biomarker method is applied to past peat deposits are: 1) each plant species deposited in the peat will contribute a plant-specific distribution of biomarkers to the peat section, 2) the compounds will survive the diagenesis mainly unchanged, and 3) the compound "assemblages" represent the past prevailing plant assemblage composition (Ficken et al., 1998; Bush and McInerney, 2013).

The geochemical plant biomarker method has been applied with promising results in bog environments (e.g. Ishiwatari et al., 2005; Jansen et al., 2006; Bingham et al., 2010). The main focus has been on identification and definition of bog plant biomarkers and in applying them to bog peat sections to track changes in the vegetation and moisture conditions (Ficken et al., 1998; Nott et al., 2000; Xie et al., 2004; Nichols et al. 2006; McClymont et al. 2008). These "bog biomarkers" have also been applied to highly decomposed permafrost fen environments (Andersson et al., 2011; Routh et al. 2014). However, because the plant assemblages between these peatland types differ significantly, the suitability of bog biomarkers as a proxy to study fen peat environments should be evaluated. To date the biomarker data is often used in combination with other proxies, such as plant macrofossils, pollen, testate amoebae or isotopes (e.g. Xie et al., 2004; Zhou et al., 2010; Andersson and Meyers, 2012).

Plant lipids as biogeochemical biomarkers

In the present study the main focus is on the lipids extracted from plant and peat samples. Lipids are substances such as fats, waxes, steroids and phospholipids, which are effectively insoluble in water but extractable by fat-dissolving solvents (Killops and Killops, 2008). In plants the lipid material is mainly concentrated on the cell walls (phospholipid bilayer) and on waxy components of the leaf cuticles, stems, spores, pollen, resinous tissues and fruits. The waxy components form a "resistant coating" against the degradation and diagenesis (breakdown of the molecules due to changes in physical conditions) of the plant macromolecules (e.g. polysaccharides, lignins, lipids, proteins), and lipids become relatively concentrated in the peat. Nevertheless, as the lipid content in plants is low, *c.* 2% of the biomass (Bliss 1962), the plant lipids represent only few percent of the total organic peat matter (Killops and Killops, 2008) and therefore may not fully reflect the organic matter sources and its preservation in peat (Zheng et al., 2007). However, plant lipids, especially *n*-alkanes derived from the waxy components of leaves and stems (Jansen et al. 2010), are one of the best preserved compounds over the geological timescale and show great potential for historical studies from peat (Bol et al. 1996). Environmental conditions, i.e. temperature, pH, soil moisture and anaerobicity, which affect the activity of the soil microorganisms decomposing the organic material, has the main influence to the preservation of the lipids in the soil (Bull et al., 2000; Dungait et al., 2012).

My study focused on the neutral lipids found in peatlands: hydrocarbons, triterpenoids, and sterols. In plants the hydrocarbons are constituents of the plant waxes. Commonly they are long chain *n*-alkanes and *n*-alcohols. The carbon chain length ranges from C_{23} to C_{35}, with odd-over-even C atoms dominating the *n*-alkanes and even-over-odd C atoms dominating the *n*-alcohols (Eglinton and Hamilton, 1967). The *n*-alkanes (normal alkanes) are the simplest acyclic straight-chain saturated hydrocarbons. Due to their covalent bonds and apolar chemistry these compounds are strong and consequently resistant to decomposition by microorganisms (Derenne and Largeau, 2001).

Triterpenoids are part of terpenoids, a class of lipids which ranges from small molecules in sex hormones to large molecules in natural rubber. All triterpenoids, such as β-amyrin and lupeol, are derived from squalene, a ubiquitous component found for instance in vegetable oils (Killops and Killops, 2008). Through diagenesis, which alters the original molecular composition, triterpenoids are most likely converted to other compounds (Pancost et al., 2002 and references therein). Sterols also belong to the class of terpenoids. Plant sterols are often referred to as phytosterols, and they include all the main higher plant sterols, such as stigmasterol and β-sitosterol, bound mainly in cell membranes and in lipoproteins (Killops and Killops, 2008). It is suggested that due to microbial activity under the anaerobic conditions of peatlands the reduction process transforms the free unsaturated sterols to saturated stanols during the early stage of diagenesis (Wakeham, 1989; Xie et al.,

2004). Therefore, the ratio of stanols to sterols increases and the ratio can be used as a proxy in tracking changes in peat decomposition (Vonk et al., 2008; Bertrand et al., 2012).

The above mentioned plant biomarker groups in plants can be separated from other organisms deposited in studied sediments for example by *n*-alkane and *n*-alcohol chain lengths as plants produce longer (> *n*-C_{22}*)* *n*-alkanes and *n*-alcohols when compared to multicellular algae and micro-organisms (< *n*-C_{22}*)*. Also, most of the triterpenoids and sterols produced by plants are not produced by other organisms (Volkman, 2005; Killops and Killops, 2008).

Most of the previous plant biomarker studies which have aimed to reconstruct past vegetation compositions and related moisture conditions, and which were carried out in bog environments, mainly focused on the differences in the *n*-alkane chain lengths of two main peat forming plant groups: *n*-C_{23} or *n*-C_{25} alkanes to indicate presence of *Sphagnum* and wet conditions, and *n*-C_{27} to *n*-C_{33} alkanes to indicate presence of vascular plants and dry conditions (e.g. Ficken et al., 1998; Nott et al., 2000; Baas et al.; 2000; Pancost et al., 2002; Nichols et al., 2006). This difference between "wet favouring *Sphagnum*" and "dry favouring vascular plants" in bogs can be expressed, for instance, using the *n*-alkane chain length ACL-value ([Σ (C_n n)/Σ (C_n)], Zhou et al. 2005). ACL is a weighted mean of the *n*-alkane chain length, which is mainly influenced by the type of vegetation and their dominating *n*-alkanes (Bush and McInerney, 2013). ACL is often also used as a palaeoclimate proxy for moisture conditions (e.g. Yamamoto et al., 2010; Zhou et al., 2010). In addition to comparing the *n*-alkane chain lengths, several previous studies have applied various *n*-alkane ratios as a proxy to infer past changes in the proportions of different plant components in peat (i.e. bryophytes, vascular plants, aquatic plants). For instance different *n*-alkane ratios e.g. *n*-C_{23}/*n*-C_{31} (Nott et al., 2000), *n*-C_{23}/*n*-C_{29} (Nichols et al., 2006), *n*-C_{25}/(*n*-C_{25}+*n*-C_{29}) (Vonk and Gustafsson, 2009) and *n*-C_{31}/*n*-C_{29} (López-Días et al., 2010) have been used to reconstruct changes of the relative abundances of *Sphagnum* mosses and vascular plants. Some previous studies have succeeded to reach a species-level, namely *Sphagnum fuscum*, with differentiations based on changes in the *n*-C_{23}/*n*-C_{25} ratio (Bingham et al., 2010). The *n*-C_{23}/ (*n*-C_{27}+*n*-C_{31}) ratio has been used to separate *Betula* spp. and *S. fuscum* (Andersson et al., 2011), and the same ratio seemed to separate fen and bog phases in permafrost environment (Andersson et al., 2011). A high ratio of *n*-C_{31}/*n*-C_{27}, originally derived from studies of non-peatland environments, is suggested to indicate important input from grass vegetation to peat deposits (Ishiwatari et al., 2005; Jansen et al., 2006). In aquatic sediments the P_{aq} ratio, which compares the abundance of short chain *n*-alkanes (*n*-C_{23}+*n*-C_{25}) to the sum of the abundances of long chain *n*-alkanes (*n*-C_{23}+ *n*-C_{25}+ *n*-C_{29}+ *n*-C_{31}), has been used to reconstruct aquatic and terrestrial plant inputs (Ficken et al., 2000; Meyers, 2003). In peatland environments this ratio has also been shown to reflect the relative abundance of *Sphagnum* mosses over the vascular plants, i.e. the habitat moisture conditions

(Nichols et al., 2006). The P_{wax} ratio compares the proportions of long chain *n*-alkanes (*n*-C_{27}+*n*-C_{29} +*n*-C_{31}) to the sum of short and long chain *n*-alkanes (*n*-C_{23}+ *n*-C_{25}+ *n*-C_{27}+ *n*-C_{29}+ *n*-C_{31}), and aims to show the relative proportion of waxy hydrocarbons over the total proportion of hydrocarbons. Similarly to previous ratios, the high P_{wax} ratio suggests a strong input from vascular plants and dry conditions, while low P_{wax} values indicate *Sphagnum* domination and wetter conditions (Zheng et al., 2007; Andersson et al., 2011). In addition to above mentioned ratios, the CPI-value can be used as an indicator of degradation processes. The CPI indicates the relative distribution of odd carbon and even carbon *n*-alkanes (Bertrand et al., 2012; Andersson and Meyers, 2012), and high CPI values have been associated with less decomposed organic material (e.g. Xie et al., 2004; Ortiz et al., 2010; Andersson and Meyers, 2012). In conclusion, all the previous studies have used ratios to separate "dry vascular favouring plants" from "wet favouring *Sphagnum* mosses", a division that may be adequate in bog peats, with microhabitats of dry hummocks where vascular plants dominate and wet hollows and lawns dominated by *Sphagnum* mosses. However, in fens the whole peatland surface is commonly relatively wet and the variation in surface vegetation, with vascular plants (mainly sedges) and *Sphagnum* mosses, is less pronounced.

The approach of relying on *n*-alkane chain lengths to reconstruct peatland changes may include additional elements of uncertainty. It is hypothesized that the long chain length *n*-alkanes protect plant leaves from water loss (Sachse et al., 2006). This is more important to the vascular plants whose leaves are constantly exposed to evapotranspiration, whereas *Sphagnum* species often live in water-saturated habitats. Moreover, in peatland environments the vascular plant roots penetrate to wet layers, and consequently the roots probably do not synthesize long chain *n*-alkanes (Huang et al., 2011). Only a few studies have considered this aspect, and addressed the potential for vascular plant leaves and roots to have different total lipid, *n*-alkane and sterol concentrations (Huang et al., 2011; Jansen et al., 2006; Pancost et al., 2002). Because roots can form a substantial part of the organic peat matter, especially in fens, it is of importance to identify their proportion in peat (Saarinen, 1996, Moore, 2002; Andersson et al., 2011, Huang et al., 2011). In my work I address this challenge.

Apart from *n*-alkanes and their ratios as the most indicative plant biomarkers, some studies have addressed the sterol composition of bog plants, focusing on *Sphagnum* mosses (Baas et al., 2000). Triterpenoids, mostly taraxer-14-ene and taraxast-20-ene, have been connected to dwarf shrubs, especially to their roots (Pancost et al., 2002). The *n*-alcohols have been recorded to have species related characteristic distributions, but they were found not distinct enough to be used in tracing vegetation changes from peat sections (Baas et al., 2000). The aim of the present work is to provide a detailed investigation of the biomarker composition of fen plants and fen peats. For this, sterols, triterpenoids and *n*-alcohols, along with the *n*-alkanes and their ratios are studied.

2 OBJECTIVES AND HYPOTHESES OF THE THESIS

The main aim of my study is to examine if the plant biomarker method is applicable in identifying past plant compositions from highly decomposed fen peat. To answer this question, I analysed both fossil peat samples and the biomarker compositions of living fen plants. My hypotheses were:

1. There are differences in the biomarker composition between different fen plants.

2. There are differences in the biomarker composition between fen and bog plants.

3. The biomarker compositions of boreal and arctic plants differ from each other due to different bioclimatic conditions.

4. Owing to differences between the biomarker compositions within and between fen and bog plants the past plant assemblages and peatland succession history can be reconstructed.

To assess whether species-specific biomarkers could be identified, and to evaluate if the fen plants differ in their biomarker composition when compared to bog plants, I analysed the biomarker composition of selected living plants collected from boreal fen (publication **I**). This information was applied to study two fossil peat sections collected from two nearby sites. To test how plant biomarkers perform in identifying plants in highly decomposed fen peat, and to evaluate how biomarker and macrofossil methods capture the major peatland regime shift from fen to bog, I used plant macrofossil and biomarker analyses in parallel (publication **II**). To investigate whether the biomarker composition of the peat forming plants reflects environmental conditions, i.e. peatland type or climate, I analysed biomarker compositions of living plants collected from an arctic peat plateau complex (publication **III**). To assess the applicability of biomarkers on highly decomposed permafrost peat, and to evaluate which of the plant proxy approaches yields the most comprehensive reconstruction of past permafrost peatland dynamics, I analysed one permafrost peat section for macrofossils and biomarkers (publication **III**).

3 MATERIALS AND METHODS

3.1 STUDY SITES AND SAMPLE COLLECTION

Siikajoki, western Finland

To define biomarkers characteristic for fen plants and to apply these to fen peat (**I** and **II**) plant and peat samples were collected from separate peatlands that are part of mire succession transects and located in the Western coast of Finland at the mid-boreal bio-climate zone (64°45´N, 24°42´E) (Fig 2.). In the area new land is constantly being exposed from the sea with rate of 9.0 mm yr^{-1} (SE 0.2 mm yr^{-1}) due to the on-going post-glacial rebound (Ekman, 1996). As a consequence, a chronosequence of terrestrial ecosystems has been formed from the coast to inland. Along this chronosequence, peatlands of different successional states occur (Tuittila et al., 2013). The peat thickness at the fen sites varied between 0.4 and 0.9 m and the water table depth is on average 10 cm below the surface (Leppälä et al., 2011; Tuittila et al., 2013).

The study sites selected for living fen plant biomarker training set (**I**) were characterized by *Carex chordorrhiza, C. rostrata, C. canescens*, *Eriophorum angustifolium*, *Comarum palustre* (syn. *Potentilla palustris*), *Menyanthes trifoliata* and bryophytes such as *Warnstorfia exannulata, Aulacomnium palustre, Sphagnum majus* and *S. riparium*. I collected 12 key fen species from three closely located fens between Siikajoki study sites SJ3 and SJ4 (Table 1, and Fig 2).

From the study sites SJ5 and SJ6 two fossil peat sections were collected to study the performance of biomarker method through fen-bog transitions (**II**). Because of the loose structure of the surface peat column the first 70 cm were collected with a box-corer. The rest of the peat sections were collected with the Russian peat corer, which enables sampling from deep layers of the peat column. The first coring site (SJ5) is a peatland in fen-bog transition stage. Vegetation at the site (SJ5) is a mosaic of wet fen communities dominated by *Sphagnum majus,* and *S. papillosum, Eriophorum vaginatum, Scheuchzeria palustris* and *Carex limosa*, and drier bog communities in hummocks dominated by dwarf shrubs *Empetrum nigrum*, *Vaccinium oxycoccos, Rubus chamaemorus,* and bryophytes *Sphagnum fuscum* and *S. balticum*. The peat core was taken from an intermediate lawn surface. The second coring site (SJ6) is a bog, which is dominated by dry hummocks with *S. fuscum, Rubus chamaemorus, Empetrum nigrum, Chamaedaphne calyculata*. The studied peat core was taken from a hummock surface.

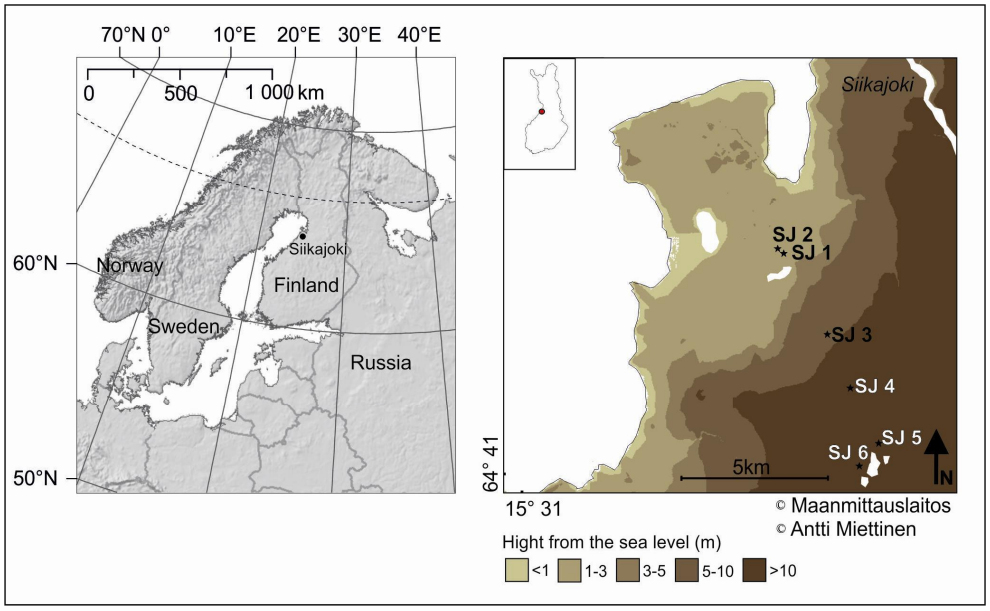

Figure 2. Location of the Siikajoki sampling site in Finland.

Figure 3. Location of the Seida sampling site in Russia (maps produced by T. Virtanen; satellite image based on QuickBird © DigitalGlobe; Distributed by Eurimage/Pöyry).

Seida, north-eastern European Russia

To extend the study to a permafrost environment (**III**), both plant and peat samples were collected from a peat plateau complex located at the discontinuous permafrost zone in arctic North-East European Russian tundra (67°03´N, 62°57´E, Seida, Komi Rebublic) (Fig 3). The highest parts of the plateau are characterized by dwarf shrubs such as *Betula nana*, *Rhododendron tomentosum* (syn. *Ledum palustre*), *Rubus chamaemorus*, and hummock mosses *Sphagnum fuscum* and *Polytrichum strictum*, while sedges, such as *Carex aguatilis* and *Eriophorum* spp., and mosses such as *Sphagnum lindbergii* dominate lower and wetter fen surfaces. One peat section was cored from a bare peat surface. Permafrost-free active peat layer (40 cm) was sampled with a Russian peat corer and the underlying permafrost peat with a motorized corer (Table 1). For the plant biomarker analyses I collected 13 plant species from fen and peat plateau habitats from the vicinity of the coring site.

3.2 BIOMARKER ANALYSIS

3.2.1 SOLVENT EXTRACTION OF LIPIDS

I studied biomarker composition of 12 boreal fen and 13 arctic fen and peat plateau plant samples, and 39 boreal and 29 permafrost peat samples (Table 1). The plant samples were first separated and washed with distilled water (**I** and **III**). Both plant and peat samples were freeze-dried and ground to a homogenous mass (**I**, **II** and **III**). Lipids were extracted from ca. 0.2 g sample mass using repeated ultrasonication (20 min) with 6 ml CH_2Cl_2/MeOH (3:1, v/v). Prior the ultrasonication the internal standards, 5-α-cholestane for apolars and 2-nonadecanone for polars, were added into the samples. Samples were saponified with 0.5 M methanolic (95%) NaOH for 2 h at 70 °C and the neutral lipids were extracted using hexane. The neutral lipids were further separated into apolar and polar compounds using activated Al_2O_3 columns, eluting with hexane/CH_2Cl_2 (9:1, v/v) and CH_2Cl_2/MeOH (1:2, v/v), respectively. Prior to analysis using gas chromatography (GC) and GC-mass spectrometry (GC-MS) the polar fractions were derivatised using bis(trimethylsilyl)trifluoroacetamide (Sigma Aldrich) (Fig 4.).

3.2.2 GAS CHROMATOGRAPHY AND MASS SPETROMETRY

Apolar and polar fractions were analysed using GC-MS with the gas chromatograph with split/splitless injection (280 ºC). Separation was achieved with a fused silica column (30 m x 0.25 mm i.d) coated with 0.25μm 5% phenyl methyl siloxane (HP-5MS), with He as carrier gas, and the following oven temperature

programme: 60 – 200 °C at 20 °C/min, then to 320 °C (held 35 min) at 6°C/min. The mass spectrometer was operated in full scan mode (50-650 amu/s, electron voltage 70eV, source temperature 230 °C). Compounds were assigned using the NIST mass spectral database and comparison with published spectra (e.g. Killops and Frewin, 1994; Goad and Akihisa, 1997). Quantification was achieved through comparison of integrated peak areas in the FID chromatograms and those of internal standards of known concentration (5-α-cholestane for apolars and 2-nonadecanone for polars). Concentration values are given as concentration per dry weight (**I**) and per TOC (**II** and **III**) of extracted material.

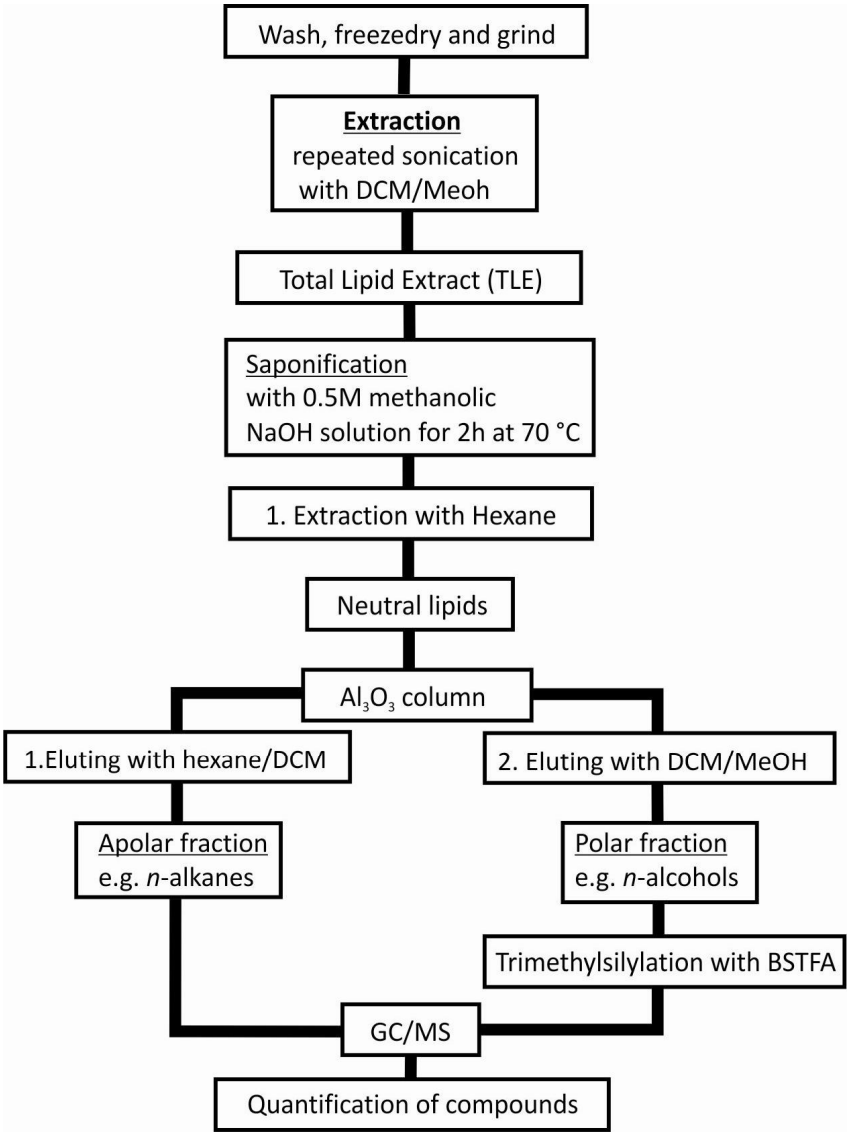

Figure 4. The biomarker analysis laboratory protocol.

3.2.3 TOTAL ORGANIC CARBON MEASUREMENTS

To make peat samples with different extent of degradation comparable between publications **II** and **III,** the biomarker concentrations were normalized to total organic carbon (TOC) content and presented as concentration per g TOC (Meyers, 2003; Ortiz et al., 2010). Total organic C and N were measured by the CHN elemental analysis (Leco TrueSpec® Micro). In the method ca. 1-2 mg freeze dried and ground sample is combusted at 950°C with He as a carrier gas. The reduction of the combustion gases is carried out in a separate furnace, and separated into individual components on a temperature programmed desorption column and fed into a thermal conductivity detector. Results are computed as concentrations of C and N from the detector signal.

3.3 PLANT MACROFOSSIL ANALYSIS

Plant macrofossil samples were taken with a varying resolution (Table 1). The sample volume was 5 cm^3 (**II** and **III**). The plant macrofossil procedure in principal follows Väliranta et al. (2007). The peat samples were rinsed under running water using a 140-µm sieve. No chemical treatment was used. The remains retained on a sieve were identified under a stereomicroscope (magnification of 10x) and proportions of different plant remains and seeds were estimated with aid of scale paper under the petri dish. If the proportion of bryophytes exceeded 10 % of the total sample volume a high power light microscope was used to identify bryophytes to species level, and to count individual proportions for different bryophyte species. Also, the proportion of unidentified organic matter (UOM) was estimated. Selected literature (e.g. Mauquoy and Van Geel, 2007; Cappers et al., 2006; Laine et al., 2009) in parallel with personal collection of M. Väliranta were used as reference for the plant and seed identification.

3.4 CHRONOLOGY

The basal ages of the studied Siikajoki peatlands were estimated based on the known land-uplift rate, *c.* 7 mm/yr (**II**) (Ekman, 1996), at the coast line of Gulf of Bothnia (Tuittila et al., 2013). Six bulk peat samples from Seida permafrost section were sent for ^{14}C analysis to Poznań Radiocarbon Laboratory Poland (**III**). The ^{14}C dating is based on the comparison of the ratio of ^{14}C to stable C (^{12}C or ^{13}C) isotopes in dead organic matter with standard ratio in modern atmosphere, which enables the determination of the radiocarbon age. Radiocarbon age represents the time passed between the death of the organism and the moment of measurement. Living organisms assimilate constant concentration of ^{14}C from atmosphere and after death

the amount of ^{14}C starts to decline due to radioactive decay. Because the natural production of radiocarbon has not been constant through time the radiocarbon ages BP (years Before Present) have to be calibrated (Cal years BP) (Pilcher J.R., 2003). In the present work the ages were calibrated with the CALIB software (Stuiver and Reimer, 1993) version 7.0.0, using the IntCal13 calibration curve (Reimer et al., 2013). The age-depth model was calculated using the method of Heegaard et al. (2005) in R (version 2.15.0) (R Development Core Team 2012).

3.5 STATISTICAL ANALYSIS

Most of the statistical analyses in the present work are multivariate ordination analyses (**I**, **II** and **III**) conducted by using Canoco for Windows versions 4.52 (**I**) and 5.0 (**II** and **III**) (ter Braak and Smilauer, 2002 and 2012). In the analyses biomarkers and macrofossils were used as response variables while one plant (**I** and **III**) or peat sample (**II** and **III**) represents individual case. For the analyses macrofossil species were expressed as relative abundances (%) and biomarker data as concentrations (**I** = μg/g dry wt., **II** and **III** = μg/gTOC).

In publication **I** RDA was used to analyse what proportion of variation in the biomarkers composition was related to different plant groups: mosses, vascular plants above- and below-ground plant parts, and to estimate the significance of the three plant groups for the variation in the biomarker distribution. For the analysis the biomarker data were centred and standardized to make different biomarkers comparable. Biomarkers that were found in less than 4 samples were omitted from the analysis. All constrained axes were tested and unrestricted Monte Carlo permutation test (a test of statistical significance obtained by repeatedly shuffling the cases) with 499 permutations was used to evaluate the statistical significance (pseudo F-value and *p*–value) of the relationship between the biomarkers and the plant groups.

In publication **II** DCA was used to quantify the variation in the macrofossil plant species in Siikajoki peat sections and to assess if macrofossils form groups by depths along the ordination axes. The macrofossil data were log transformed and rare species were down-weighted to stabilize the data before the analysis runs. Detrending was conducted by segments, to cope with the possible arch effect in the data and to make the recovered compositional gradient straight (linear). To quantify the variation in Siikajoki peat profile biomarkers and to assess if biomarkers form groups by depths the biomarker compositions were analysed by using PCA with centred and standardized data. Finally I tested if the variation in biomarkers in the peat sections correlates with the variation in macrofossil data by conducting a RDA for biomarkers where case scores from macrofossil DCA ordination were used as explanatory variables. The biomarker data was centred and standardized and all

constrained axes were tested with unrestricted Monte Carlo permutation (number of permutations 499). TWINSPAN analysis (see below) was applied to combined macrofossil and biomarker data to define those macrofossils and biomarkers that occur together.

In publication **III** PCA was applied to study the variation of biomarkers within the studied living arctic plants. First a PCA with all defined biomarker groups (sterols, *n*-alcohols, triterpenoids, *n*-alkanes and *n*-alkane ratios) was conducted. Then, the variation in the four compound groups (sterols and triterpenoids, *n*-alcohols, *n*-alkanes and *n*-alkane ratios) was analysed independently to compare how well they separate the studied plant species apart when used separately. For the analysis biomarker data were log transformed, centred and standardized. To inspect if the variation in peat biomarker data related to variation in plant macrofossil data in the peat profile another PCA was applied. In this PCA the sample-depth groups, which were based on macrofossil compositions defined by TWINSPAN-analysis (see below), were used as nominal supplementary variables to determinate whether the peat biomarkers show specific compounds for macrofossil depth groups. The supplementary variables in the analysis are not used in the ordination solution, but projected passively into the ordination space based on the results (Lêps and Ŝmilauer, 2003).

TWINSPAN (Two Way INdicator SPecies ANalysis, Twinspan for Windows 2.3) was applied in publications **II** and **III**. The aim of the TWINSPAN is to produce species classification according to their ecological preferences (Hill and Šmilauer, 2005). The classification of cases is based on species typical appearance of one part of the division and consequently these species can be considered as indicators of particular ecological conditions (Lêps and Ŝmilauer, 2013). In current study individual peat sample represent one case and macrofossils and biomarkers within the sample represents species (**II** and **III**). Prior to TWINSPAN analyses all macrofossil abundances (**II** and **III**) and the biomarker concentrations (**II**) were rescaled from 0 to 1 by setting the highest unit for each plant/biomarker species to 1 and calculating other values as percentage of the highest abundance of the unit. In the analysis (**II** and **III**) was used five cut levels (0.0, 0.2, 0.4, 0.6 and 0.8) of abundance and two division levels, which determinate the maximum level of recursive splitting for samples and for species (Hill and Šmilauer, 2005). Basic correlation analyses in publications **I** and **II** were conducted by SPSS PASW statistics 18.

Table 1. Details of the sampling sites, sampling resolution and used methods and analysis.

Study site	**(I) Sitkajoki, Finland**	**(II) Sitkajoki, Finland**	**(III) Seida, Komi Republic, Russia**
Corrdinates	**64°45´N, 24°42´E**	**64°45´N, 24°42´E**	**67°03´N, 62°57´E**
Site description	**Fen:** *Carex* spp., *Eriophorum angustifolium*, *Warnstorfia* spp., *Sphagnum* spp., *Comarum palustre* (syn. *Potentilla palustris*), *Menyanthes trifoliata*	**Fen-bog transition peatland (SJ5)**: *Eriophorum vaginatum, Scheuchzeria palustris, Carex limosa, Rubus chamaemorus, Empetrum nigrum, Vaccinium oxycoccos, Sphagnum* spp. **Bog (SJ6):** *S. fuscum, Rubus chamaemorus, Empetrum nigrum, Chamaedaphnea calaculata*	**Peat plateau:** *Betula nana, Rhododendron tomentosum* (syn. *Ledum palustre*), *Rubus chamaemorus, S. fuscum, Polytrichum strictum, Dicranum elongatum* **Fen:** *Carex aquatilis, Eriophorum* spp., *S. lindbergii*
Sampled plants	*S. papillosum, S. fimbriatum, S. subsecundum, S. riparium, Warnstorfia exannulata, C. livida, C. nigra, C. rostrata, C. lasiocarpa, Eriophorum angustifolium, Menyanthes trifoliata, Comarum palustre*		*Lichen* spp., *Dicranum elongatum, S. fuscum, S. balticum, S. lindbergii, Eriophorum sp., C. aquatilis, B. nana, Rubus chamaemorus, Betula pubescens ssp. czerepanovii syn. tortuosa, Vaccinium uliginossum, Rhododendron tomentosum (syn. Ledum palustre),*
Core information	-	**SJ5:** 6-150 cm **SJ6:** 0-100 cm	0-166 cm
Analysis	**Biomarkers (TLE)**	**Biomarkers, Macrofossils**	**Biomarkers, Macrofossils, ^{14}C**
Sampling information	**Plants:** bryophytes were treated as whole plants, vascular plants were divided into above- ground and below-ground parts	**Biomarkers** **SJ5** selected samples cm: 22, 26, 30, 32, 36, 40, 42, 46 cm resolution 10 cm: 50-150 cm **SJ6** selected samples cm: 52, 56, 60, 62, 66, 70, 72, 76 cm resolution 10 cm: 0 - 50; 80 - 100 cm **Macrofossils** **SJ5** resolution 2 cm: 0-50 cm resolution 10 cm: 50-150 cm **SJ6** resolution 2 cm: 40-80 cm resolution 10 cm: 0-40; 80-100 cm	**Biomarkers** **Plants:** bryophytes treated as whole plants, vascular plants divided into leaves and roots, tree *Betula* divided into leaves, bark and wood matter **Peat** cm: 0, 8, 12, 16, 22, 24, 28, 32, 36, 40, 44, 48, 52, 56, 64, 72, 80, 96, 104, 112, 120, 128, 136, 144, 152, 160, 166 **Macrofossils** cm: 0, 4, 8, 12, 16, 20, 22, 24, 28, 32, 36, 40, 44, 48, 52, 56, 64, 68, 72, 76, 80, 84, 88, 92, 96, 100, 104, 108, 112, 120, 124, 128, 132, 136, 140, 144, 148, 152, 156, 160, 164, 166 **^{14}C** cm: 0, 26, 54, 82, 110, 138, 160
Statistical analysis	**RDA**	**PCA, RDA, DCA, TWINSPAN**	**PCA, TWINSPAN**

4 RESULTS

4.1 BIOMARKER COMPOSITION OF THE LIVING PLANTS

The plan biomarker composition of studied fen plants led to the rejection of hypothesis 1, as the plant biomarker composition of studied plants did not allow species level identification of fen plants. However, by using *n*-alkanes, *n*-alkane ratios, sterols and triterpenoids in combination, the different plant groups could be separated: mosses and vascular plants, and below- and above-ground parts of vascular plants (**I**: Fig 5 a, b; **III**: Fig 2). The *n*-alkanes and their ratios were statistically the most significant group of biomarkers that separated mosses and vascular plants. Sterols and triterpenoids provided additional information separating vascular plant below- and above-ground parts and mosses apart, while the *n*-alcohols between studied plants did not differ significantly.

In the fen environment the *n*-alkanes appeared promising in separating *Sphagnum* mosses and above-ground parts of vascular plants but less promising in separating mosses and below-ground parts of vascular plants. Fen *Sphagnum* mosses were dominated by mid chain alkanes *n*-C_{23} and *n*-C_{25} whereas fen vascular plants above-ground parts were dominated by long chain alkanes *n*-C_{27} to *n*-C_{33}. However, the *n*-alkane distribution and concentrations of the below-ground parts of sedges and *M. trifoliata* resembled those of *Sphagnum* mosses (**I**). Because of this similarity the most common *n*-alkane ratios (e.g. *n*-C_{23}/*n*-C_{25}) that have been used in bog environments to separate vascular plants from *Sphagnum* mosses no longer performed satisfactory when below-ground parts were included into the analysis. The observed similarity was clearer in boreal fen plant samples (**I**: Fig 4) than in arctic site plants. At the arctic site the high concentration of mid-chain *n*-alkanes in *Betula pubescens* ssp. *czerepanovii*, syn. *tortuosa* leaves overlapped with those of *Sphagnum* mosses (**III**: Supplementary Information Table 1).

In addition to the dominance of specific *n*-alkanes, the ratios of different *n*-alkanes could be used to identify plant groups. Some statistically significant *n*-alkane ratios were detected, which separated fen plant groups. Ratios *n*-C_{25}/*n*-C_{29}, *n*-C_{23}/*n*-C_{27}, *n*-C_{23}/ (*n*-C_{27} + *n*-C_{31}), P_{aq} and P_{wax} separated *Sphagnum* mosses from vascular plants (**I**: Fig 4), while high ratios of *n*-C_{23}/ *n*-C_{21} for *B. pubescens* ssp. *czerepanovii* and *B. nana* leaves separated them from other arctic plants. The two main groups, *Sphagnum* mosses and vascular plants, were also clearly separated by *n*-alkane ratios that were not statistically the most significant ones, such as ACL, *n*-C_{31}/*n*-C_{29} and *n*-C_{31}/*n*-C_{27} (**III**: Supplementary Information Table 1).

Sterols and triterpenoids appeared to be useful for identification of plant groups. β-sitosterol and phytol were found in much higher concentrations in vascular plant leaves, lupeol was found in roots, and brassicasterol, campesterol, obtusifoliol and gramisterol were found in *Sphagnum* mosses (**I**). These differences in sterol and triterpenoid composition between fen *Sphagnum* mosses and the above- and below-ground parts of vascular plants, if detected, could be used in separating these two components in peat.

Hypothesis 2 was also rejected when considering the biomarker composition of vascular plants and *Sphagnum* mosses, since they did not clearly differ between fen and bog plants. In the fen environment the most significant biomarkers separating *Sphagnum* mosses from vascular plants were the same as in previous studies in bog environments: mid chain *n*-alkanes dominated *Sphagnum* and long *n*-alkanes dominated vascular plants (**I** and **III**) (e.g. Ficken et al., 1998; Nott et al., 2000; Baas et al.; 2000; Pancost et al., 2002; Nichols et al., 2006).

Hypothesis 3 was also rejected using the data presented in this study. Instead of the expected geographical differences in biomarker composition between sites, the chemical structures of the studied arctic peat plateau plants resembled those of boreal or temperate peatlands, indicating that plants from different bioclimatic zones have uniform biomarker compositions (**III**). Results showed similar biomarker composition in the studied arctic plants as in the corresponding plants in boreal and temperate zones.

4.2 PLANT BIOMARKERS IN THE PEAT ARCHIVES

Based on the plant macrofossil analyses the studied peat sections were divided into different peatland habitats. The boreal peat profiles (Siikajoki SJ6 and SJ5) included fen, fen-bog transition and bog phases. In addition, the bog phases included hummock and lawn microhabitats, respectively (**II**: Fig 2). The permafrost peat profile from (Seida) included swamp fen, fen and bog phases (**III**: Fig 3). The lower fen layers were more decomposed than those in the upper part of the bog sequences in both boreal and arctic peat sections, as indicated by the high amount of unidentified organic matter (UOM), low percentages of identified plant remains, and low C/N ratio, together with the biomarkers which can be used as measures of degradation of organic matter (CPI and 5α(H)-stanol/Δ^5-sterol ratio) (**II**: Fig 9, **III**: Supplementary Information Table 2).

Plant biomarkers were consistently found through the studied peat sections, and also from the highly humified fen layers. The results thus partly support hypothesis 4: past plant assemblages and peatland succession histories can be reconstructed due to differences in fen and bog plant biomarker compositions. When biomarkers were used as a single proxy to study the peat composition, a rough division by depths

occurred. However, because this division could not be linked to any specific plant species or plant groups *per se*, no profound conclusions on past habitat types or moisture conditions could be drawn based solely on the biomarker record. When the biomarker and macrofossil data were combined more confidence was gained in the connection of the plant biomarker distribution and different peatland habitats (**II**: Fig 7; **III**: Fig 5).

In the Siikajoki peat sections, the RDA (pseudo F = 9.2, *p*-value = 0.002), where the biomarker and the macrofossil data were combined, indicated that the *n*-alkanes *n*-C_{20}, *n*-C_{22}, *n*-C_{24}, *n*-C_{26}, *n*-C_{27}, *n*-C_{28}, 22E-stigmastanol and 3-stimastanol concentrations decreased in association with the shift from fen (with e.g. *M. trifoliata, Sch. palustris, Equisetum* spp. and sedges) to bog habitats (with shrubs and *Sphagna*). Typical biomarkers for lawn habitats (with *S. magellanicum* and *S. papillosum*) were, for instance, *n*-C_{23}/*n*-C_{27} and *n*-C_{31}/*n*-C_{29}, and for hummock habitats (with *S. fuscum, S. angustifolium* and dwarf shrub roots and leafs) *n*-C_{25}, *n*-C_{29}, and *n*-C_{28}-alcohol. The analysis did not detect any characteristic biomarkers which would describe statistically significantly the fen-bog transition zone.

In the Seida permafrost peat section the PCA, which combined the biomarker and the macrofossil data, indicated some habitat specific biomarkers (**III**: Fig 5). Swamp fen layers, with woody and herbaceous plant remains, clearly stood out and they were characterised by *n*-alkanes C_{34} and C_{35}, the *n*-C_{31}/ *n*-C_{27} ratio, and taraxast-20-ene and phytol. In contrast, the biomarkers derived from the sedge-*Menyanthes*-dominated fen layers were randomly scattered in the ordination space. The bog habitat, with *Sphagnum* spp., lichens and dwarf shrub remains, was separated from the other two habitats but none of the biomarkers described it.

In addition to statistical observations, clear patterns in the biomarker distribution in the studied peat sections were detected. The long-chain odd *n*-alkanes (*n*-C_{27} to *n*-C_{31}) appeared to be typical for the vascular plant-dominated fen sections both in Siikajoki and Seida, whereas *n*-C_{23} and *n*-C_{25} alkanes dominated the bog *Sphagnum* layers (**II**: Fig 4 a and b, **III**: Supplementary Information Table 2). In the Siikajoki peat sections (SJ6 and SJ5) many *n*-alkane ratios such as *n*-C_{23}/*n*-C_{27}, *n*-C_{23}/*n*-C_{29}, *n*-C_{31}/*n*-C_{27} and *n*-C_{31}/*n*-C_{29} showed changes from the base of the peat profile towards the top, reflecting the peatland succession from fen to bog. The high *n*-C_{23}/*n*-C_{25} ratio on the top part of the SJ6 hummock core corresponds to the prevalence of *Sphagnum fuscum*. This ratio remained low in the wet lawn top layers of SJ5 core (**II**: Fig 5) where *S. fuscum* was lacking. In the Seida peat section most of the studied *n*-alkane ratios suggested rather unchanged conditions throughout the peat accumulation history, apart from a *ca*. 20 cm deep layer in the middle of the section where the ratios momentarily increased (**III**: Supplementary Information Figure 2). Simultaneously the dominance of the long chain length *n*-alkanes in peat were replaced by mid chain length *n*-alkanes with clearly lower concentrations. These biomarkers imply presence of *Sphagnum* mosses, sedge roots or *Betula* leaves. In

this particular layer the amount of UOM was lower than in the rest of the section and the macrofossil samples contained high amounts of sedge and shrub root remains.

The sterol and triterpenoid compositions of fossil peat did not reflect the plant-specific biomarker compositions that were found from living fen plants. Compounds such as brassicasterol, campesterol, stigmasterol and β-sitosterol, with the associated stanols, characterised Siikajoki peat sections. The highest concentrations of sterols, stanols, and taraxer-14-ene and taraxast-20-ene were detected at the close vicinity of the fen-bog transition zone where also high amounts of sedge roots and UOM were encountered (**II**: Fig 6). The biomarker based degradation measures, CPI and 5α(H)-stanol/Δ^5-sterol ratio, also showed changes around the transition zone (**II**: Fig 9). In the Seida section β-sitosterol and related 3-stigmastanol were present throughout the section, with no clear changes in their concentrations. Campesterol and the related stanol were present from the middle section to the top, but stigmasterol and the related stanol were found only from the very top layers. Unlike in Siikajoki sections, the Seida section sterols and triterpenoids did not show changes at the very thin fen-bog transition layer which was detected at the very top of the section by the macrofossil record, as sedge remains and appearance of *Sphagnum* mosses (**III**: Supplementary Information Table 2). The *n*-alcohol distributions showed no substantial changes in the studied peat cores.

5 DISCUSSION

5.1 BIOMARKER COMPOSITION OF LIVING PLANTS

Most of the previous studies on plant biomarkers have concentrated specifically on the *n*-alkane composition in plants and in peat, and mainly bog plants have been analysed (e.g. Ficken et al., 1998; Nott et al., 2000; Baas et al., 2000; Pancost et al., 2002; Nichols et al., 2006). In contrast only a few studies have reported sterol or triterpenoid composition in living plants (Baas et al., 2000; Pancost et al., 2002). Although the *n*-alcohols have been studied, they were found not to be distinctive enough to be applicable in tracing plant compositions from peat (Baas et al., 2000). Consequently, the most useful group of biomarkers to study bog histories has been the *n*-alkanes (Table 2).

In the current study the *n*-alkanes and the *n*-alkane ratios proved to be statistically the most significant markers to separate living fen plant groups, and in particular to separate *Sphagnum* mosses and vascular plants above- and below-ground parts (**I**: Fig 5, **III**: Fig 2), while species-level identification of the plants was not achieved. No clear differences between the biomarkers of *Sphagnum* and vascular plants living in fen or bog environments were discovered either. In other words, the biomarker composition of the studied fen plants corresponded to those of bog plants: long chain length *n*-alkanes (*n*-C_{27} to *n*-C_{33}) dominate vascular plants such as sedges, forbs, dwarf shrubs and *Betula*, and lichen, whereas the mid chain length *n*-alkanes (*n*-C_{23} and *n*-C_{25}) dominate *Sphagnum* mosses. My results also agree with the prevailing view that different *n*-alkane ratios can be used to separate contributions originating for different plant groups (Nott et al., 2000; Ishiwatari et al., 2005; Jansen et al., 2006; Nichols et al., 2006; Zheng et al., 2007; Vonk and Gustafsson, 2009; Bingham et al., 2010; Andersson et al., 2011). However, importantly, my results showed that when a wider combination of living plants from fens and bogs, as well as different below- and above-ground plant parts are incorporated, the absolute values behind the *n*-alkane ratios can drastically change. This may influence and even bias the data interpretation.

The chemical differences detected between *Sphagnum* mosses and above-ground vascular plant parts, as well as the similarities between *Sphagnum* and below-ground vascular plant parts, could originate from the hydrological conditions of the habitat (Sachse et al., 2006). It is hypothesized that the main physiological function of long chain *n*-alkanes in leaf cuticles is to reduce water loss (e.g. Eglinton and Hamilton, 1967). *Sphagnum* mosses and vascular plant roots typically occupy the wet peat surface and layers under the peat surface. Thus, there is no need for protective long chain *n*-alkane structures to reduce water loss when compared to leaves (Huang et al., 2011, **I**). Moreover, Diefendorf et al. (2011) detected that the *n*-alkane concentration of the evergreen plant leaves was almost a double when compared to

the leaves of deciduous plants within the same functional group (angiosperm). Hence, fen and bog vascular plants differ substantially e.g. in their leaf structure, as dwarf shrubs which dominate bog hummock surfaces commonly have evergreen leaves while many fen plants such as sedges and forbs are deciduous, it can be hypothesized that fen vascular plants do not produce similar amounts of protective *n*-alkanes compared to dwarf shrubs which are exposed to evapotranspiration through many seasons. Accordingly, to trace plant species from highly decomposed fen peat layers, which are dominated by remains of deciduous plants, by using biomarkers, is a challenging task.

In previous studies plant biomarkers from the boreal zone have been used in arctic peat (e.g. Routh et al. 2014; Andersson et al., 2011). Current results that showed no difference in the plant biomarker composition between arctic and boreal zone plants give justification for this procedure. My results on living plant biomarkers suggest that the biomarker composition of plants is not associated to bioclimatic factors (**III**).

5.2 APPLICABILITY OF PLANT BIOMARKERS FOR RECONSTRUCTING THE SUCCESSION HISTORY

Plant biomarkers occurred consistently in the studied peat sections, also in highly decomposed fen peat layers, but if the biomarker data were solely used a less detailed picture emerged and reliable conclusion about the historical plant assemblages could not be drawn (**II** and **III**). However, biomarker records supported the macrofossil observations when these data sets were combined in the ordination analysis (**II**: RDA, **III**: PCA). Biomarker data described different peatland habitats; in Siikajoki: bog hummocks and lawns, and fens (**II**: Fig 7), in Seida: swamp fen and fen sections (**III**: Fig 5). Several biomarkers were also able to indicate that changes had occurred along the studied peat sections.

The boreal peat sections showed similar biomarker compositions as suggested by previous studies: the hummock peat layers including dwarf shrub macrofossils were dominated by *n*-C_{31}, which is an indicator of dwarf shrubs (e.g. Pancost, 2002), while the presence of *S. fuscum* was indicated by the low ratio of *n*-C_{23}/*n*-C_{25} (Bingham et al., 2010). Lawn layers, dominated by *S. magellanicum* and *S. papillosum,* were described by *n*-C_{23}, *n*-C_{25} and *n*-C_{31} alkanes similarly to Bingham et al. (2010). Ratios *n*-C_{23}/*n*-C_{25} and *n*-C_{23}/*n*-C_{31} were said to describe dry bog environments (Bingham et al., 2010), and consistently in the current study these ratios described the dry hummock but not the wetter lawn environment (**II**). The transition zone between fen and bog habitat was characterized by a shift from long-chain *n*-alkanes in fen layers to mid-chain *n*-alkanes in bog peat layers. High concentrations of sterols and triterpenoids clearly reflect the presence of sedges (e.g.

Pancost et al., 2002; **I**; **II**). Another characteristic feature was the changes in degradation measures in the transition zone, such as higher concentrations of stanols, decreased ratio of 5α(H)-stanols/Δ^5-sterol, describing anoxic conditions and decay of plant material (Bertrand et al., 2012), and increase in CPI value, indicating better preservation of organic matter at the top bog layers and a progressive degradation in fen layers (Andersson and Meyers, 2012).

In the Seida permafrost peat section statistically significant biomarkers for swamp fen and fen layers could be identified (**III**: Fig 5). Results agreed with the previous study of Andersson et al (2011) which suggested that e.g. higher P_{aq} (0.6-0.7) values described a fen phase in a permafrost environment. In the current study low P_{aq} values also corresponded with the fen phase. Andersson et al. (2011) proposed that the n-C_{23} /(n-C_{27} + n-C_{31}) ratio differentiates fen and bog habitats in arctic peats. When this ratio was applied to the current Seida peat section it identified the wet fen phase but failed to identify the drier swamp fen phase, which was in contrast classified as a bog phase. In conclusion, the ratio performed better as an indicative marker for changes in moisture conditions rather than being an indicator of a peat type; fen *vs*. bog (**III**). The Seida macrofossil record suggested a thin bog peat layer at the very top but the biomarker record did not support this. Unlike macrofossils, the biomarkers did not show any indications of fen-bog transition (**III**), which is contrary to the case of boreal Siikajoki sections (**II**). Also, biomarkers indicated the possible presence of *Sphagnum* mosses in the fen layers while no fossil plant remains were detected by the macrofossil method. The same biomarkers could also reflect the presence of sedge roots (**I**) detected by using the macrofossil record (**III**). The presence of *Sphagnum* in the historical community was very likely because several *Sphagna* species are currently present among fen vegetation in Siikajoki and in Seida. Conclusively, there were cases where biomarkers provided additional information from highly humified peat when compared to macrofossils.

Although the study on biomarker distributions of the living fen plants (**I**) suggested that sterols and triterpenoids could provide more information about the fossil plant assemblages, this assumption proved premature when fossil peat samples were analysed. In all studied peat sections, the sterols such as brassicasterol, campesterol, stigmasterol and β-sitosterol, which were common in most of the studied living plants, were found throughout the peat sections. However, those compounds that were indicative for instance for sedge roots (lupeol) or *Sphagnum* mosses (obtusifoliol and gramisterol) (**I**) were not detected from fossil peat layers, even though macrofossil records showed presence of these plant remains. In the fen peat layers the saturated stanols (campestanol, 22E-stigmastanol and 3-stigmastanol) of the common sterols were statistically more significant compounds to describe the fen environment than their counterpart sterols. The absence of the plant-specific sterols is presumably due to degradation (Bertrand et al., 2012; Andersson and Meyers, 2012) and the down-core appearance of stanols indicates an increase in degradation level of organic matter since deposition. Consequently, it seems that

sterols and stanols are not applicable to infer plant-specific information; rather they are approximations of the level of degradation and diagenesis of the compounds along the section.

The changes in the dominating *n*-alkane chain length appeared to be most useful in separating different peatland habitats; long chain length *n*-alkanes dominated fen layers and mid chain length *n*-alkane dominated bog layers. The *n*-alkane ratios also changed along the peat sections. These biomarkers suggested *Sphagnum* domination in the surface (i.e. bog environment) in Siikajoki and vascular plant domination in the deeper sections (i.e. fen environment) both in Siikajoki and Seida sites (**II** and **III**) (e.g. Ficken et al., 1998; Nott et al., 2000: Baas et al., 2000; Pancost et al., 2002; Nichols et al., 2006). An alternative interpretation to such a change has also been proposed: the down-core shift in the dominating chain length has been speculated to result from the compound degradation. Typically the decomposition of the major *n*-alkane homologue increases downwards in the core and this is characterized by a change through *n*-C_{25} and *n*-C_{27} to *n*-C_{31} alkane, where shorter chain homologues disappear during diagenesis (Lehtonen and Ketola, 1993). Thus it can be speculated that the presence and higher concentrations of the longer-chain *n*-alkanes in the bottom fen peat sections is a result of compound degradation rather than absence of mid-chain *n*-alkanes denoting *Sphagnum* mosses. On the other hand Schellekens and Buurman (2011) reported a down core increase of *n*-C_{23} and decrease of summed *n*-C_{29} and *n*-C_{31} alkanes, while the amount of *Sphagnum* decreased. They suggested this to indicate that the chain length reduction occurs during the diagenesis under anaerobic conditions in peat dominated by higher plants. In the light of current results from living fen plants, an explanation to this chain length shift could be the presence of vascular plant roots. In the current study the macrofossil record also suggested the absence of *Sphagnum* mosses in the vascular plant dominated peat layers, and thus supported the interpretation of the plant group specific *n*-alkane being deposited in peat layers rather than being driven by decomposition of the compounds.

In bogs, which are characterized by dry and wet microhabitats, biomarkers perform well and a distinction between mosses and vascular plants can be achieved - even to a species-level identification of mosses in some studies (Bingham et al., 2010). In contrast to bogs, southern boreal fen environments do not have clear microhabitats and related differences in moisture conditions, hence information about different plant groups, such as sedges, forbs, dwarf shrubs and wood (which indicate different moisture conditions), should be more robust. This kind of information would be highly important when reconstructing past CO_2, CH_4 and N dynamics from fen environments (Larmola et al., 2014; Levy et al., 2012; Laine et al., 2007; Riutta et al., 2007). Based on this study it has to be concluded that in highly humified fen environments plant biomarkers did not provide reliable information about the historical plant assemblages. Even in highly humified permafrost environment, where plant macrofossils were scarce, the plant

macrofossils basically provided the most essential information but that biomarker analysis should not be neglected as a complimentary proxy to yield additional information

5.3 FUTURE PROSPECTS

In the future, macrofossil and biomarker analyses could be complemented by additional analyses to attain more accurate information of historical fen peat layer vegetation. For example, the pyrolysis method can be used to trace the lignin products that are absent in *Sphagnum* but rich in non-*Sphagnum* species (McClymont et al., 2011; Weng and Chapple, 2010). By studying the concentrations of the neutral monosaccharides *Sphagnum* mosses, vascular plants and lichens could be separate more accurately (Jia et al. 2008). The thermally assisted hydrolysis and methylation (TMAH) procedure could also give more accurate information about the contributions from *Sphagnum*-mosses (Abbott et al. 2013). Another potential way to differentiate *Sphagnum* mosses, sedge roots and *Betula* leaves is the determination of compound-specific (e.g. *n*-C_{23}) δD (deuterium) values of different plants, plant parts and peat *n*-alkanes, in order to decipher water source and the contemporary hydrological environment (e.g. Xie et al., 2004; Nichols et al., 2009; Garcin et al., 2012). Moreover, δD could also perform as a potential climate proxy in estimating the amount of precipitation and temperature as wet and dry climate periods (e.g. Xie et al., 2000 and 2004; Sachse et al., 2006; Nichols et al., 2006; Garcin et al., 2012; Seki et al. 2012). The $\delta^{13}C$ signatures could be used to determine the origin of different compounds, in order to explore the diagenesis process in a more detailed way (Meyers 2003). In addition, $\delta^{13}C$ values when isolated from plant remains could be used to some extent to reconstruct past atmospheric CO_2 concentrations (White et al., 1994; Figg and White, 1995). The testate amoebae analysis could be added as an additional proxy to provide more information of the past changes in the moisture conditions and type of vegetation (Nichols et al., 2006; Charman et al., 2007; Väliranta et al., 2011).The UOM peat component (together with lost material due the rinsing of the samples with 140 μm sieve), which is high in fen peat sections, might deserve more attention in the future. UOM includes decayed plant material that cannot be identified under a microscope. It is difficult to reliably compare the vegetation data derived from humified phases with biomarker results, because biomarker analyses are carried out from bulk peat samples that include all peat fractions (Ficken et al., 1998). One option, although it is relatively laborious, would be to separate the identifiable and un-identifiable material apart prior to the biomarker analysis and focus the biomarker analysis on the UOM part.

Because in general the biomarker method is relatively laborious and time-consuming, and laboratory procedures are expensive, the analyses are commonly performed without replication. In many other fields of ecological studies repetition and replicates are highly important and demanded by the research community. Moreover, in biomarker data analyses statistical methods (as undertaken here) are seldom applied to test the significances of the detected patterns. This tradition probably stems from the lack of replicated analyses. If biomarkers are to remain as a common proxy in palaeoecological studies a greater amount of replicates and exploitation of suitable statistical analyses are recommended in order to achieve more confident results.

Table 2.Overwiev of the dominant *n*-alkanes of studied living plants.

Mosses		**Shrubs**		**Sedges, grasses**		**Forbes**	
Sphagnum		*Empetrum nigrum*	C31 a and C29 k	*Carex* sp.	C33 e	*Osmunda regalis*	C31 h
S.magellanicum	C31 b, g and C25 c, f, g,	*E.nigrum* L	C31 l	*C. bigelowii*	C27 a	*Pteridium aquilinum* L	C27 h
S.imbricatum	C23 c, d	*E.nigrum* L	C29 l	*C.canescens*	C27 h	*Pteridium aquilinum* S	C27 h
S.palustre	C23 b, c, i	*B.nana* L	C27 l	*C.aryi* L	C31 j	*Dryopteris* sp. L	C25, C27 j
S.papillosum	C23 b, c, g, m and C25 f	*B.nana* R	C29, C27 l	*C.aryi* R	C31 j	*Dryopteris* sp. R	C27, C29, C31 j
Rigida		*Ledum palustre*	C29 k	*C.doniana* L	C29 j	*Caltha palustris*	C25 k
S.compactum	C25 c and C32 h	*L.palustris* L	C31 l	*C.doniana* R	C31 j	*Sanguisorba officinalis* L	C33 j
Acutifolia		*L.palustris* R	C29 l	*C.dimorpholepi* L	C27 j	*Sanguisorba officinalis* R	C33 j
S.capillifolium	C31 a, b and C25 f	*Rhodoadendro groenlandicum*	C31 e	*C.dimorpholepi* R	C33 j	*Menyanthes trifoliata* L	C27 j and C29 m
S.fimbriatum	C25 c, m	*Vaccinium uliginosum* L	C27 l	*C.rochebrunl* L	C31 j	*Menyanthes trifoliata* R	C25 j and C21 m
S.fuscum	C25 a, f, g, l	*Vuliginosum* R	C27, C29 l	*C.rochebrunl* R	C31 j	*Comarum palustre*	C33 (C31) k
S.molle	C25 c	*Erica tetralix*	C31 b	*C.aquatilis* L	C27 l	*P.palustris* L	C31 m
S.rubellum	C25 c, g and C31 d	*E. tetralix* fine R	C33 d	*C.aquatilis* R	C27 l	*P.palustris* R	C31 m
S.subnitens	C23 h	*E. tetralix* coarse R	C31 d	*C.livida* L	C27 m	*Geranium wilfordii* L	C31 j
Cuspidata		*E. tetralix* S	C31 d	*C.livida* R	C21 m	*Geranium wilfordii* R	C35 j
S.angustifolium	C25 f and C23 g	*E.mackaiana* L	C31 h	*C.nigra* L	C27 m	*Polygonum paleceum* L	C27 i
S.balticum	C31 f and C23 g, l	*E.mackaiana* S	C31 h	*C.nigra* R	C27 m	*Polygonum paleceum* R	C29, C33 j
S.cuspidatum	C31 b, h and C23 c, d, g	*Calluna vulgaris*	C31 b, h	*C.lasiocarpa* L	C31 m	*Euphorbia esula* L	C31 j
S.lindbergii	C25 f and C23 g, l	*C. vulgaris* L	C33 d	*C.lasiocarpa* R	C23 m	*Euphorbia esula* R	C31 j
S.majus	C31 f and C23 g	*C. vulgaris* S	C29 h	*C.rostrata* L	C29 m	*Veratrum nigrum* L	C31 j
S.pulchrum	C23 c	*C. vulgaris* R	C31 d	*C.rostrata* R	C23 m	*Veratrum nigrum* R	C31 j
S.recurvum	C23 b, c	*C. vulgaris* S	C33 d	*Eriophorum* sp. L	C29 l	*Rubus chamaemorus* L	C27 l
S.riparium	C23 m	*Vaccinium itis-idaea*	C29 a and C31 k	*Eriophorum* sp. R	C27 l	*Rubus chamaemorus* R	C27, C29 l
S.tenellum	C23 c, g	*Vaccinium oxycoccos*	C29 b	*E.vaginatum*	C31 b	*Rubus arcticus*	C29 k
Subsecunda		*Vocxy. microcarpus*	C29 k	*E.angustifolium* L	C27 m	*Rubus saxatilis*	C29 k
S.subsecundum	C25 h and C23 m	*Adromedia polifolia*	C31 b and C29 k	*E.angustifolium* R	C27 k and C31 b	*Dryas octopetala*	C31 k
S.denticulatum	C23 h	*Kalmia polifolia*	C29 e	*E.angustifolium*	C27 k and C31 b	*Rumex cf. arcticus*	C27, C29 k
		Arctous alpina	C31 k	*Trichophorum cespitosum*	C31 b		
Racomitrium lonuginosum	C31 a	*Vaccinium myrtillys*	C31 k	*Rhynchospora alba*	C31 b,h		
Polytrichum sp.	C31 b	*Chamaedaphneo calyculata*	C29 e	*Juncus effusus* L	C31 j and C23 h		
Pol. formosum	C29 e	*Ulex europaeus* L	C29 h	*J.effusus* S	C29 h		
Pol.commune	C31 l and C33 i	*Ulex europaeus* S	C27 h	*J.effusus* R	C31 j		
Dicranum elongatum	C31 l			*J.articulatus*	C31 h		
Aulacomnium palustre	C27 b and C29 i			*Hierochloe pauciflora*	C27 k		
Hypnum revolutum	C27 i			*Molinia caerulea*	C29 h		
Hypnum revolutum	C33 i			*Molinia* sp.	C31 h		
Hypnum cupressiforme	C29 b						
Camplylopus introflexus	C27 h						
Camplylopus pyriformis	C29 h						
Warn.exannulata	C27 m						
Other		**Deciduous trees**		**Coniferous trees**			
Cladonia sp.	C31 a, b, l	*Betula pubescens ssp. czerepanovii*		*Juniperus* cf. *Davurica*	C33 k		
Drosera intermedia	C27 h	*syn. Tortuosa* L, B, WM	C27 l	*Larix dahurica*	C31 k		
Hyperzia selago	C29 a	*B.exilis*	C27 k	*Pinus pumila*	C27 k		
Spiraea cf. *media*	C29 k	*B.fructicosa*	C27 k	*Pinus subirica*	C31 k		
		Alnus viridis	C27 k	*Pinus banksiana*	C29 n		
		Salix sp.	C27 k	*Picea glauca*	C29 n		
		Cornus alba	C28 k				
		Cotoneaster cf.melanocarpus	C29 k				
		Populus tremuloides	C25 n				

Big letters are abbreviations; L: leaves, S: stems, R: roots, B: bark and WM: wood matter. Small letters (a to n) refer to references: a: Ficken et al. 1998; b: Nott et al. 2000; c: Baas et al . 2000; d: Pancost et al. 2002; e: Nichols et al. 2006; f: Vonk and Gustafsson 2009; g: Bingham et al. 2010; h: Ortiz et al. 2011; i: Huang et al. 2012; j: Huang et al. 2011; k: Tarasov et al. 2013, m: Ronkainen et al. 2013; n: Norris et al. 2013.

6 CONCLUSIONS

- The plant biomarker analyses of living fen plants indicated that *n*-alkanes and their ratios are the most useful markers to separate plant groups: *Sphagnum* mosses and vascular plants.

- Biomarker compositions did not differ substantially between the same species living on fens and bogs.

- The species-specific biomarker compositions of living plants derived from different bioclimatic zones did not differ, suggesting that, at least to some extent, local plant biomarker training sets can also be applied beyond the geographical area where they were created.

- When a wider combination of plants, plant parts and peatland environments are incorporated both in the training set and down-core record, the interpretation of the biomarker data become more challenging. Thus, a use of a larger set of valid proxies is advisable to study past peat layers and changes in deposition environment.

- Throughout the peat sections, from highly humified fen peat layers to the topmost bog peat layers, the macrofossil method proved to be the most competitive proxy to reconstruct past vegetation assemblages and local environmental conditions.

- Biomarkers, when interpreted in parallel with macrofossil data, were able to reflect the major changes in the dominating plant groups and in the moisture conditions. Accordingly they separated the important bog microhabitats: hummocks and lawns and showed the major regime shifts from fen to bog.

- The biomarker method, as applied here, performs best as a complimentary proxy when used in combination with macrofossils. Thus, if applied as a single proxy, the results should be interpreted cautiously.

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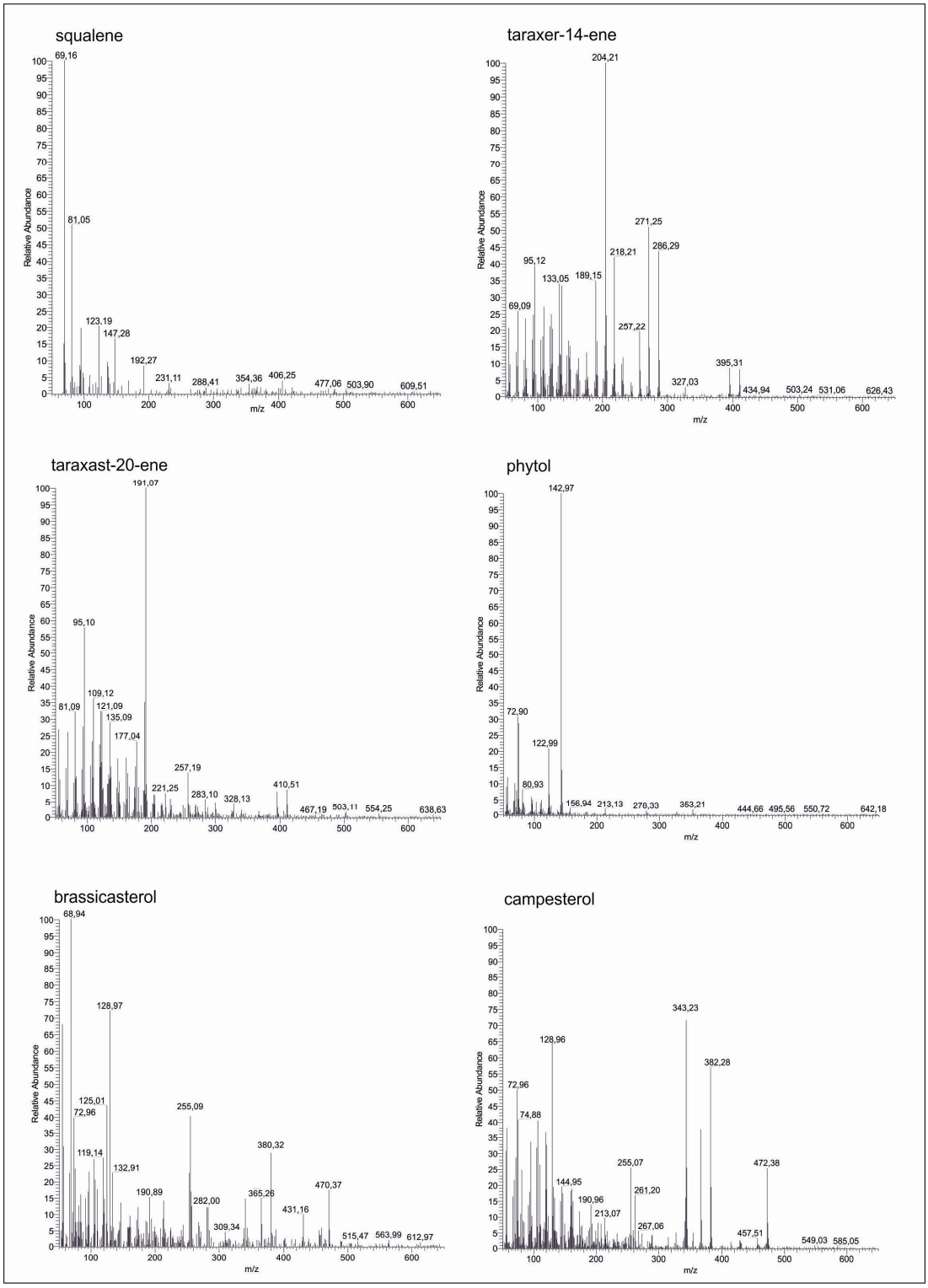
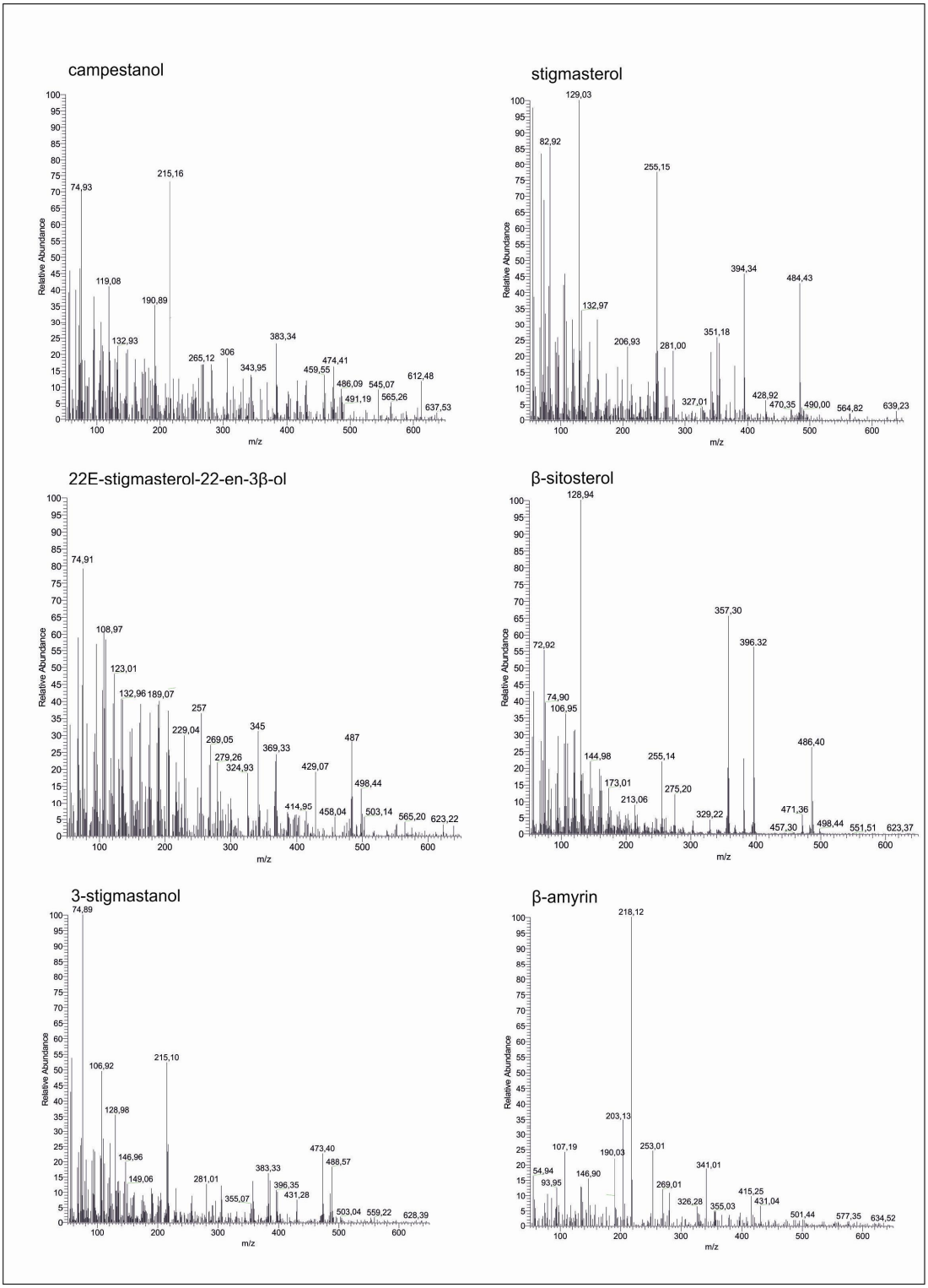
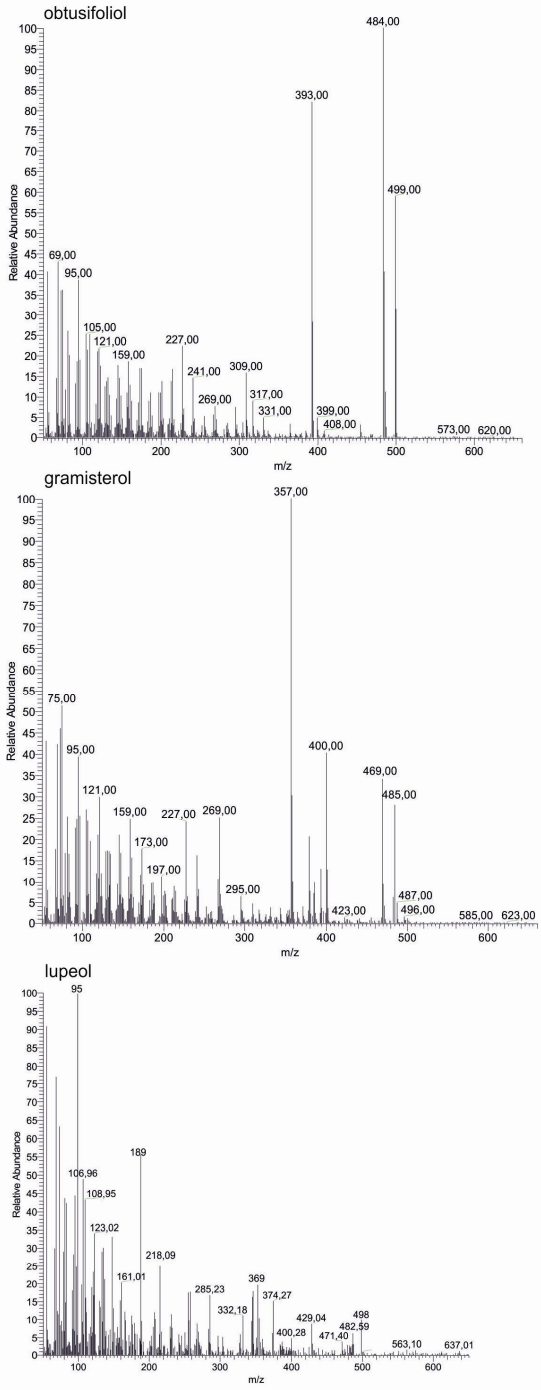
APPENDIX

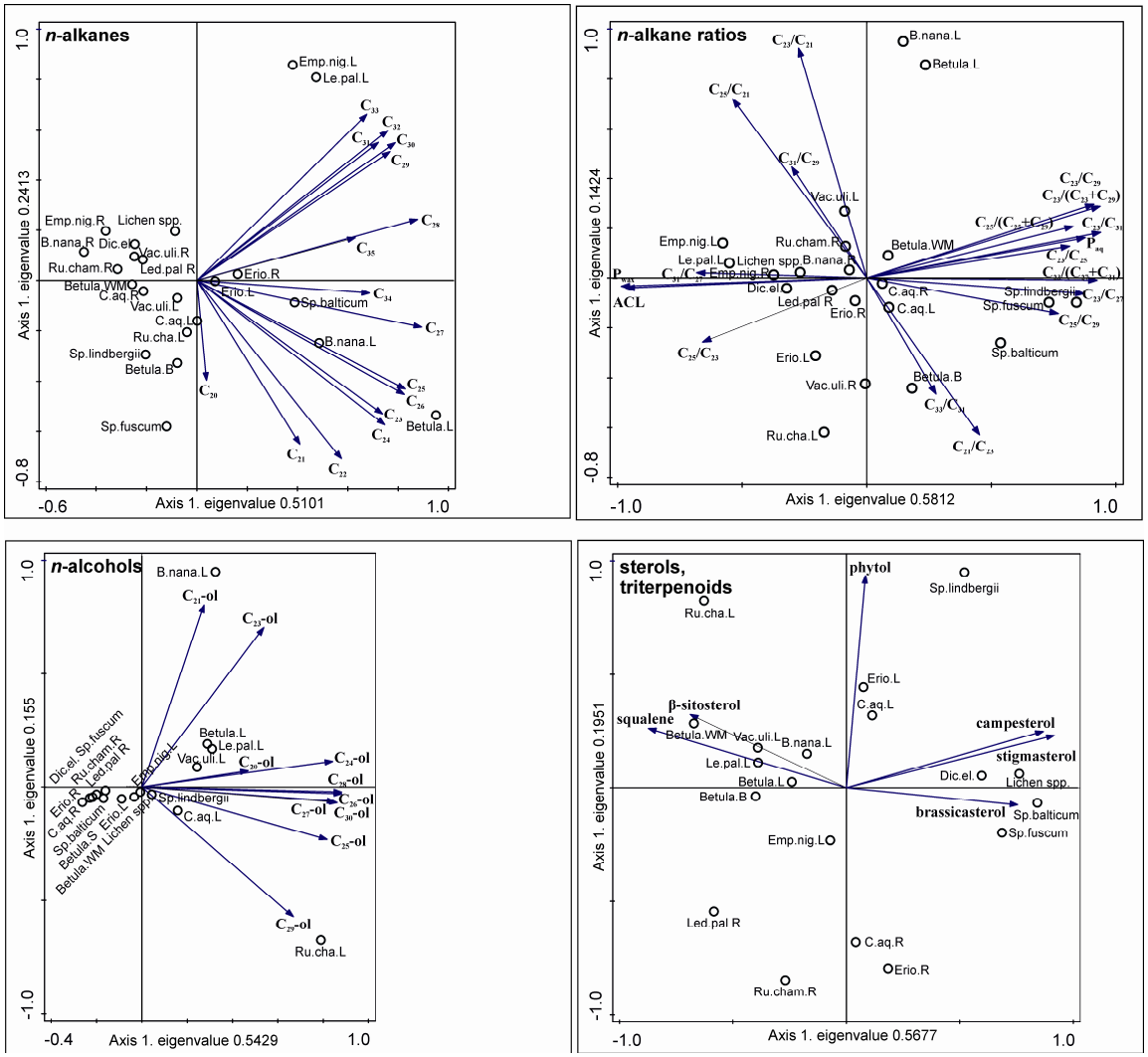
Mass spectrometry m/z figures of the triterpenoids, sterols and stanols (common names) found in the samples in their appearing order.



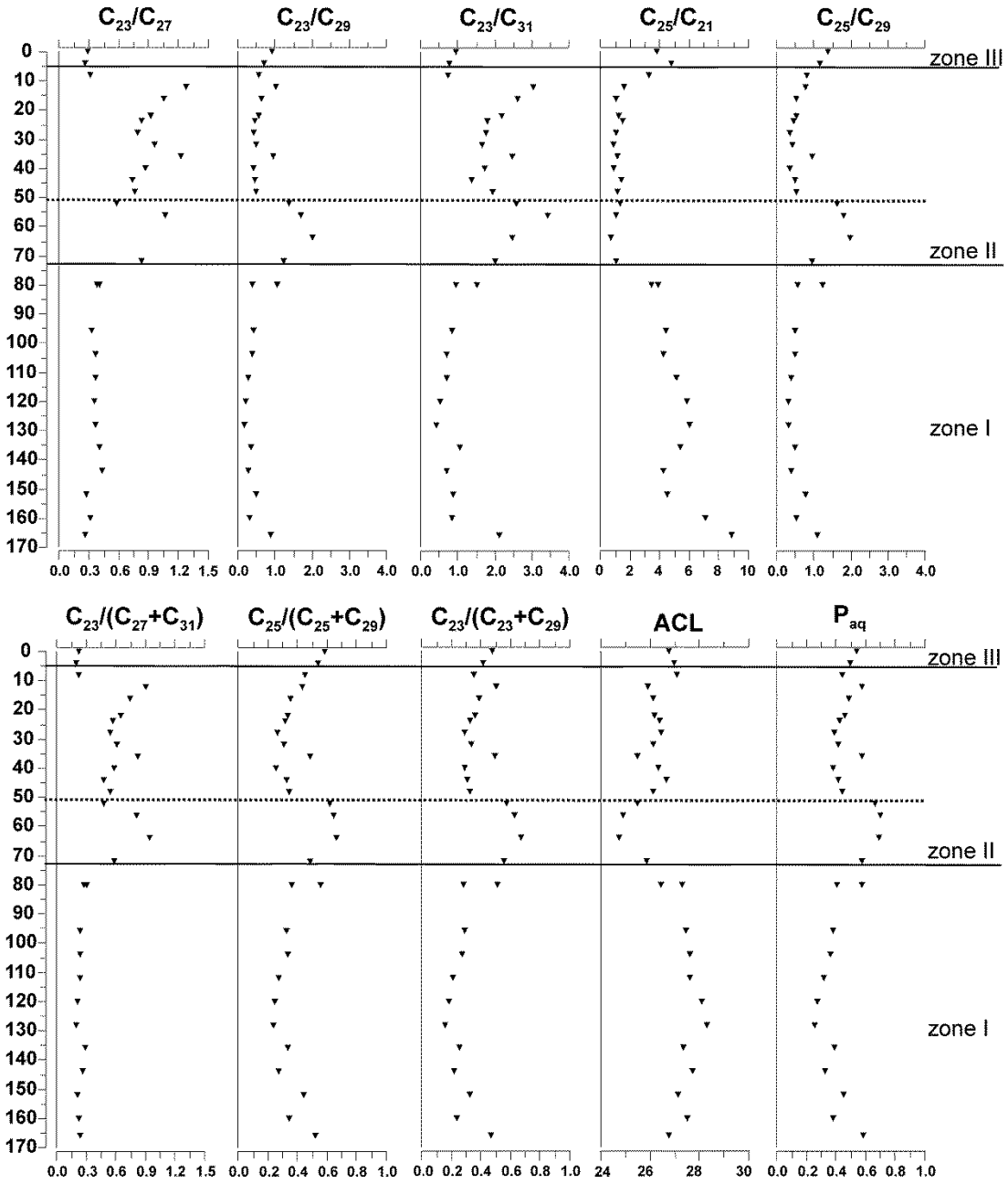

campestanol
Relative Abundance
m/z
74,93
215,16
119,08
190,89
132,93
265,12
306
343,95
383,34
459,55
474,41
486,09
491,19
545,07
565,26
612,48
637,53
stigmasterol
129,03
82,92
255,15
132,97
206,93
281,00
351,18
394,34
484,43
327,01
428,92
470,35
490,00
564,82
639,23
22E-stigmasterol-22-en-3β-ol
74,91
108,97
123,01
132,96
189,07
257
229,04
269,05
279,26
324,93
345
369,33
429,07
414,95
458,04
487
498,44
503,14
565,20
623,22
β-sitosterol
128,94
357,30
396,32
72,92
74,90
106,95
144,98
255,14
173,01
213,06
275,20
329,22
486,40
471,36
457,30
498,44
551,51
623,37
3-stigmastanol
74,89
106,92
215,10
128,98
146,96
149,06
281,01
355,07
383,33
396,35
431,28
473,40
488,57
503,04
559,22
628,39
β-amyrin
218,12
203,13
107,19
190,03
253,01
54,94
93,95
146,90
269,01
341,01
326,28
355,03
415,25
431,04
501,44
577,35
634,52


obtusifoliol
Relative Abundance
m/z
484,00
393,00
499,00
69,00
95,00
105,00
121,00
159,00
227,00
241,00
309,00
269,00
317,00
331,00
399,00
408,00
573,00
620,00
gramisterol
Relative Abundance
m/z
357,00
75,00
95,00
121,00
159,00
227,00
269,00
173,00
197,00
295,00
400,00
469,00
485,00
423,00
487,00
496,00
585,00
623,00
lupeol
Relative Abundance
m/z
95
189
106,96
108,95
123,02
218,09
161,01
285,23
369
374,27
332,18
429,04
498
482,59
400,28
471,40
563,10
637,01

Supplementary Information for publication III



Supplementary Information Figure 1. PCA of living plant biomarkers: for *n*-alkanes first two axes explain 75% of the variation; for *n*-alkane ratios first two axes explain 72% of the variation; for *n*-alcohols ratios first two axes explain 69% of the variation; for sterols and triterpenoids first two axes explain 76 % of the variation.



Supplementary Information Figure 2. 10 best fitted (PCA for peat ratios) *n*-alkane ratios of peat sequence. Marked zones according to the macrofossil data; I: swamp fen, II: fen, III: bog. Dashed line marks zone within fen zone where UOM is low and amount of sedges is high.

Publication III. Supplementary Information Table 1. Plant biomarker data.

Plant samples		*n*-alkanes																	
Sample	Habitat	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	C35
Betula tree L	mineral soil	nd	nd	0,5	17,9	21,0	1141,6	88,5	1510,2	96,6	2565,1	34,4	319,7	24,3	248,0	11,0	21,3	6,6	2,6
B.nana L	peat plateau hummock	nd	nd	0,2	6,3	7,4	489,8	33,6	550,3	29,9	844,7	20,0	171,9	13,5	306,6	9,0	29,7	1,2	0,8
Rubus chameamorus L	peat plateau hummock	nd	nd	0,7	1,5	11,4	2,3	14,0	24,7	11,9	43,7	11,9	21,9	4,4	9,6	4,4	4,5	2,2	1,7
Carex aquatilis L	fen	nd	0,8	0,6	3,8	2,8	18,4	14,9	17,5	13,2	58,2	13,3	27,1	7,2	8,8	4,4	3,1	2,7	1,6
Eriophorum sp. L	fen	nd	nd	0,4	4,8	2,0	12,5	11,3	31,8	11,1	66,5	12,3	101,4	8,1	40,6	4,4	5,3	3,5	2,0
Vaccinium uliginossum L	peat plateau hummock	nd	nd	nd	0,4	1,2	9,2	15,8	42,9	11,4	127,0	11,9	15,7	6,5	7,3	3,1	3,3	1,8	1,4
Ledum palustre L	peat plateau hummock	nd	nd	nd	0,9	0,9	11,8	8,1	40,9	12,1	102,3	34,5	1448,0	66,1	1623,1	47,4	355,0	2,4	1,9
Empetrum nigrum L	peat plateau hummock	nd	nd	nd	0,5	0,7	7,2	6,1	24,3	6,5	156,4	20,0	852,8	47,3	1552,3	40,5	539,9	3,7	2,2
B.nana R	peat plateau hummock	nd	nd	0,2	0,3	0,7	2,9	4,7	5,2	4,2	6,9	6,3	7,2	4,9	5,9	2,9	2,1	1,3	0,9
R. chameamorus R	peat plateau hummock	nd	nd	0,1	0,3	1,2	4,3	8,0	8,5	7,7	10,9	7,6	10,7	6,1	8,1	2,7	3,3	1,5	0,9
C.aquatilis R	fen	nd	nd	0,2	0,9	1,5	6,6	10,8	11,5	11,0	13,9	9,6	10,4	6,2	5,8	3,5	3,1	2,0	1,1
Eriophorum s p. R	fen	nd	nd	0,3	2,6	2,5	14,1	14,0	24,9	16,7	45,6	18,9	40,1	13,4	20,0	9,6	6,0	4,9	2,1
V. uliginossum R	peat plateau hummock	nd	nd	nd	nd	1,3	4,4	8,4	8,4	8,6	10,0	11,3	10,0	7,8	8,1	4,2	2,9	2,1	0,9
L. palustre R	peat plateau hummock	nd	nd	0,3	0,9	1,0	4,6	7,7	10,1	10,6	12,0	10,0	17,2	6,9	15,1	4,1	3,3	1,3	1,6
E. nigrum R	peat plateau hummock	nd	nd	0,2	0,3	0,8	2,5	5,3	5,5	5,3	8,2	7,0	68,8	3,5	46,4	2,5	3,5	1,2	0,7
Betula tree WM	mineral soil	nd	0,1	0,2	0,6	1,6	6,7	7,3	12,1	7,0	15,9	13,4	9,1	4,9	4,2	3,3	1,7	1,9	1,1
Betule tree B	mineral soil	1,9	4,1	6,0	8,2	5,7	9,2	11,4	14,4	9,3	24,3	8,0	10,7	8,9	7,8	5,0	3,4	2,9	1,4
Lichen spp.	peat plateau hummock	nd	0,2	0,2	0,5	1,2	4,0	7,6	10,3	11,2	15,7	12,3	24,9	9,6	31,8	4,9	9,2	2,8	2,0
Dicranum elongatum	peat plateau hummock	nd	0,3	0,2	0,8	1,0	4,0	8,3	9,6	8,6	10,5	5,8	34,4	5,6	59,3	3,2	11,6	1,5	0,8
Sphagnum fuscum	peat plateau hummock	nd	0,3	0,2	86,9	4,1	103,5	11,5	133,6	11,2	59,5	5,0	11,8	2,1	9,4	1,5	2,3	1,6	0,5
Sp.balticum	fen	nd	2,1	0,6	38,7	3,7	66,4	14,1	44,2	18,4	33,2	28,2	27,4	24,0	21,0	13,5	9,5	6,9	4,7
Sp.lindbergii	fen	nd	0,7	0,2	20,2	2,8	45,4	8,1	21,8	8,7	11,7	7,9	7,8	4,1	4,8	2,8	2,2	1,9	0,9

Tree *Betula* = *Betula pubescens* ssp. *Czerepanovii,* syn. *Tortuosa*
not detected = nd
sample omitted = -
L = leaves WM = wood matter
R = roots B = bark

n- alkane ratios

Sample	C23/C25	C23/C27	C23/C29	C23/C31	C25/C29	C31/C27	C31/C29	C33/C31	C23/ (C23+C29)	C25/ (C25+C29)	C23/ (C27+C31)
Betula tree L	0,8	0,4	3,6	4,6	0,6	0,1	0,8	0,1	0,8	0,8	0,4
B.nana L	0,9	0,6	2,8	1,6	0,7	0,4	1,8	0,1	0,7	0,8	0,4
R. chameamorus L	0,1	0,1	0,1	0,2	0,6	0,2	0,4	0,5	0,1	0,5	0,0
C. aquatilis L	1,0	0,3	0,7	2,1	0,3	0,2	0,3	0,4	0,4	0,4	0,3
Eriophorum sp. L	0,4	0,2	0,1	0,3	0,5	0,6	0,4	0,1	0,1	0,2	0,1
V. uliginossum L	0,2	0,1	0,6	1,3	0,3	0,1	0,5	0,5	0,4	0,7	0,1
L. palustre L	0,3	0,1	0,0	0,0	0,4	15,9	1,1	0,2	0,0	0,0	0,0
E. nigrum L	0,3	0,0	0,0	0,0	0,2	9,9	1,8	0,3	0,0	0,0	0,0
B.nana R	0,6	0,4	0,4	0,5	0,7	0,8	0,8	0,4	0,3	0,4	0,2
R. chameamorus R	0,5	0,4	0,4	0,5	0,8	0,7	0,8	0,4	0,3	0,4	0,2
C.aquatilis R	0,6	0,5	0,6	1,1	0,8	0,4	0,6	0,5	0,4	0,5	0,3
Eriophorum s p. R	0,6	0,3	0,4	0,7	0,5	0,4	0,5	0,3	0,3	0,4	0,2
V. uliginossum R	0,5	0,4	0,4	0,5	0,8	0,8	0,8	0,4	0,3	0,5	0,2
L. palustre R	0,5	0,4	0,3	0,3	0,8	1,3	0,9	0,2	0,2	0,4	0,2
E. nigrum R	0,5	0,3	0,0	0,1	0,7	5,6	0,7	0,1	0,0	0,1	0,0
Betula tree WM	0,6	0,4	0,7	1,6	0,8	0,3	0,5	0,4	0,4	0,6	0,3
Betule tree B	0,6	0,4	0,9	1,2	0,6	0,3	0,7	0,4	0,5	0,6	0,3
Lichen spp.	0,4	0,3	0,2	0,1	0,7	2,0	1,3	0,3	0,1	0,3	0,1
D. elongatum	0,4	0,4	0,1	0,1	0,9	5,6	1,7	0,2	0,1	0,2	0,1
Sp. fuscum	0,8	1,7	8,8	11,0	2,2	0,2	0,8	0,2	0,9	0,9	1,5
Sp.balticum	1,5	2,0	2,4	3,2	1,3	0,6	0,8	0,5	0,7	0,6	1,2
Sp.lindbergii	2,1	3,9	5,8	9,4	1,9	0,4	0,6	0,5	0,9	0,7	2,8

								Sterol/triterpenoid				
Sample	Paq	ACL C19-C35	Pwax	C23/C21	C21/C23	C25/C21	C25/C23	squalene	taraxer-14-ene	phytol	brassica-sterol	campe-sterol
Betula tree L	0,8	26,0	0,5	63,9	0,0	84,5	1,3	160,0	nd	nd	nd	nd
B.nana L	0,7	26,4	0,6	77,5	0,0	87,1	1,1	31,3	nd	nd	nd	nd
R. chameamorus L	0,5	27,5	0,7	1,5	0,7	16,0	10,6	449,7	nd	nd	nd	nd
C. aquatilis L	0,5	26,9	0,7	4,9	0,2	4,7	1,0	21,0	nd	nd	nd	212,7
Eriophorum sp. L	0,2	28,0	0,8	2,6	0,4	6,6	2,5	16,3	nd	5209,0	nd	55,7
V. uliginossum L	0,7	26,8	0,7	23,1	0,0	107,9	4,7	190,7	nd	7309,5	nd	827,5
L. palustre L	0,0	30,2	1,0	13,2	0,1	45,6	3,5	73,1	nd	4835,7	nd	704,8
E. nigrum L	0,0	30,5	1,0	15,7	0,1	52,9	3,4	13,5	nd	284190,2	nd	nd
B.nana R	0,4	28,1	0,7	9,3	0,1	16,4	1,8	92,7	nd	nd	-	-
R. chameamorus R	0,4	28,0	0,7	16,1	0,1	32,2	2,0	1,1	nd	1647,4	nd	28,0
C.aquatilis R	0,5	27,3	0,6	7,7	0,1	13,3	1,7	9,1	nd	10575,3	nd	nd
Eriophorum s p. R	0,4	27,6	0,7	5,5	0,2	9,7	1,8	18,0	nd	1460,4	68,1	nd
V. uliginossum R	0,4	27,9	0,7		0,0		1,9	210,5	nd	-	-	-
L. palustre R	0,3	28,3	0,8	5,1	0,2	11,3	2,2	211,1	nd	1215,3	68,6	3172,6
E. nigrum R	0,1	29,4	0,9	9,9	0,1	21,7	2,2	414,4	nd	-	-	-
Betula tree WM	0,6	27,0	0,6	10,7	0,1	19,3	1,8	327,2	nd	nd	nd	257,8
Betule tree B	0,6	26,2	0,6	1,1	0,9	1,8	1,6	13,9	nd	nd	nd	nd
Lichen spp.	0,2	29,1	0,8	7,7	0,1	20,0	2,6	nd	nd	828,1	2994,7	3831,5
D. elongatum	0,1	29,6	0,9	5,0	0,2	12,1	2,4	nd	12,5	122409,4	nd	87996,1
Sp. fuscum	0,9	24,2	0,3	1,2	0,8	1,5	1,3	nd	2,2	893,2	nd	nd
Sp.balticum	0,7	25,5	0,4	1,7	0,6	1,1	0,7	nd	nd	646,6	nd	nd
Sp.lindbergii	0,8	24,4	0,3	2,2	0,4	1,1	0,5	nd	nd	nd	nd	126,7

				n-alcohols										
Sample	stigma-sterol	**β**-sitosterol	3-stigma- stanol	C20-ol	C21-ol	C22-ol	C23-ol	C24-ol	C25-ol	C26-ol	C27-ol	C28-ol	C29-ol	C30-ol
Betula tree L	nd	70343,8	1465,1	124,5	nd	nd	nd	79,9	nd	nd	nd	nd	nd	nd
B.nana L	nd	6609,5	290,4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
R. chameamorus L	nd	2600,4	277,9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
C. aquatilis L	nd	7707,1	673,1	nd	nd	nd	nd	213,6	nd	420,0	nd	983,0	nd	1517,4
Eriophorum sp. L	nd	nd	nd	242,6	18,5	1177,4	97,5	1153,0	nd	491,6	44,8	541,4	nd	66,3
V. uliginossum L	246,2	17494,8	326,9	nd	nd	nd	nd	60,7	nd	108,9	nd	122,6	nd	nd
L. palustre L	214,6	6192,5	131,9	nd	nd	nd	nd	86,7	nd	346,8	72,4	7457,9	nd	220,9
E. nigrum L	nd	139915,0	nd	1134,0	nd	2589,1	nd	11608,9	778,1	82238,3	1981,1	52463,2	832,6	5781,2
B.nana R	-	-	-	-	-	-	-	-	-	-	-	-	-	-
R. chameamorus R	nd	2989,5	80,0	26,5	nd	1792,0	73,1	768,3	61,5	346,3	56,8	326,0	nd	19,3
C.aquatilis R	nd	5210,3	nd	221,4	nd	135,8	11,9	864,1	33,6	619,2	106,5	652,1	nd	nd
Eriophorum s p. R	nd	3307,8	nd	35,3	nd	101,6	nd	513,8	nd	386,8	nd	191,9	nd	nd
V. uliginossum R	-	-	-	-	-	-	-	-	-	-	-	-	-	-
L. palustre R	2791,0	3994,3	nd	nd	nd	nd	nd	31,2	nd	nd	nd	nd	nd	nd
E. nigrum R	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Betula tree WM	24,9	4814,4	90,6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Betule tree B	nd	26757,1	nd	39,2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Lichen spp.	10807,4	1546,6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
D. elongatum	70963,1	50805,9	nd	nd	nd	nd	nd	3768,4	nd	4604,0	nd	1467,6	nd	nd
Sp. fuscum	nd	288448,1	58609,5	1082,6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sp.balticum	nd	54058,6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sp.lindbergii	66,2	4348,4	136,9	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Publication III. Supplementary Information Table 2. Peat sequence biomarker data.

Peat samples					Sterol/triterpenoid									
Depth	C%	C/N	Bulk density	CPI	squalene	taraxer-14-ene	urs-12-ene	taraxast-20-ene	phytol	campe-sterol	campe-stanol	stigma-sterol	22E-stigmasterol-22-en-3β-ol	β- sitosterol
0 cm	52,6	23,4	0,16	7,5	0,9	15,5	2,9	3,8	nd	1388,7	nd	663,5	nd	10791,6
4 cm	53,0	24,0	0,15	7,1	0,3	7,9	2,8	4,0	-	-	-	-	-	-
8 cm	51,5	22,8	0,10	6,7	1,1	4,7	2,0	2,0	136,1	244,4	nd	71,9	nd	2735,2
12 cm	51,1	22,3	0,09	5,3	2,2	nd	nd	1,6	34,8	106,1	56,4	nd	nd	686,4
16 cm	52,4	19,8	0,07	3,6	69,6	nd	5,4	2,0	178,9	136,1	87,5	nd	nd	808,6
22 cm	52,9	18,5	0,08	5,0	0,9	nd	2,2	3,3	915,6	301,9	229,2	nd	nd	3064,6
24 cm	53,2	19,4	0,07	5,0	nd	nd	1,6	3,4	156,4	113,5	99,2	nd	nd	769,5
28 cm	54,0	19,0	0,10	4,9	1,1	nd	5,3	4,7	296,1	175,2	131,6	nd	nd	1012,0
32 cm	53,0	19,2	0,09	4,6	0,5	nd	5,0	5,4	165,6	129,4	73,5	nd	nd	663,3
36 cm	52,2	19,0	0,12	3,3	0,6	nd	2,7	7,0	536,2	202,2	186,2	88,3	135,1	1187,6
40 cm	50,6	18,9	0,09	4,8	0,3	nd	1,9	9,2	140,2	85,7	59,5	nd	nd	659,4
44 cm	51,6	19,7	0,14	2,2	1,0	nd	2,0	10,0	150,9	101,7	nd	nd	nd	528,5
48 cm	52,3	20,1	0,07	4,4	0,5	nd	2,5	7,7	336,8	nd	nd	nd	nd	1043,1
52 cm	49,7	22,5	0,00	3,8	2,1	nd	1,6	4,3	159,2	434,1	nd	nd	nd	14020,1
56 cm	44,1	22,2	0,08	2,4	1,9	nd	1,5	4,4	12,7	42,6	35,8	nd	nd	787,3
64 cm	48,5	24,1	0,07	2,3	2,3	nd	nd	6,5	113,0	420,4	293,8	nd	nd	2782,2
72 cm	43,4	20,2	0,06	3,2	0,9	nd	0,9	5,3	98,7	214,1	113,5	nd	nd	1006,3
80 cm	43,4	21,9	0,08	10,9	1,2	nd	2,7	4,8	345,3	nd	nd	nd	nd	1540,7
88 cm	39,6	19,4	0,06	3,2	0,7	nd	2,3	8,1	-	-	-	-	-	-
96 cm	31,0	25,7	0,16	6,1	0,7	nd	nd	7,7	374,7	nd	nd	nd	nd	2483,6
104 cm	43,1	22,1	0,08	6,7	1,0	nd	4,2	10,8	227,9	nd	nd	nd	nd	612,1
112 cm	47,6	21,4	0,08	6,4	1,6	nd	nd	11,3	453,7	nd	nd	nd	nd	1202,9
120 cm	42,7	21,9	0,08	5,3	0,8	nd	nd	8,1	169,4	nd	nd	nd	nd	521,1
128 cm	40,7	19,9	0,08	5,9	1,1	nd	nd	4,6	148,4	135,8	nd	nd	nd	804,4
136 cm	44,1	23,5	0,10	6,6	1,1	nd	nd	5,4	162,6	nd	nd	nd	nd	1478,6
144 cm	42,0	22,1	0,09	3,3	0,7	nd	nd	7,5	148,7	nd	nd	nd	nd	1013,2
152 cm	14,3	18,5	0,25	3,2	nd	nd	nd	4,6	440,0	nd	nd	nd	nd	4281,2
160 cm	26,7	17,6	0,18	3,2	nd	nd	nd	5,3	142,5	nd	nd	nd	nd	1813,4
166 cm	14,9	19,5	0,00	4,7	nd	nd	nd	3,4	104,8	nd	nd	nd	nd	913,9

not detected = nd
sample omitted = -
C22-ol concentrations are omitted from the analysis due contamination of the detected peak in GC-MS

			n-alcohols									
Depth	3-stigmastanol	3-stigmastanol/ β-sitosterol	C20-ol	C21-ol	C22-ol	C23-ol	C24-ol	C25-ol	C26-ol	C27-ol	C28-ol	C30-ol
0 cm	2107,7	0,2	1284,0	405,4	-	707,1	5392,6	313,1	3387,5	360,1	2884,8	274,2
4 cm	-		-	-	-	-	-	-	-	-	-	-
8 cm	699,4	0,2	344,3	80,9	-	106,3	1046,0	46,1	679,1	62,1	478,6	55,2
12 cm	272,1	0,3	37,0	5,2	-	nd	63,1	nd	49,5	nd	58,6	nd
16 cm	522,5	0,4	48,0	14,6	-	14,7	110,6	nd	126,2	nd	124,8	nd
22 cm	1481,2	0,3	300,6	69,2	-	nd	1671,3	88,9	1160,8	90,5	715,9	120,3
24 cm	485,9	0,4	45,0	10,4	-	nd	90,2	nd	86,1	nd	72,8	nd
28 cm	886,5	0,5	79,4	11,9	-	15,4	222,0	nd	189,2	nd	140,2	74,1
32 cm	610,5	0,5	29,6	7,9	-	nd	81,6	nd	89,8	nd	97,3	23,6
36 cm	986,6	0,5	168,5	32,7	-	43,0	1511,3	51,3	1355,6	53,0	978,3	167,9
40 cm	671,6	0,5	27,1	15,1	-	nd	80,9	nd	143,5	nd	127,5	nd
44 cm	459,7	0,5	24,0	20,0	-	nd	55,4	nd	81,1	nd	93,3	nd
48 cm	911,0	0,5	nd	nd	-	nd	165,6	nd	248,2	nd	193,7	nd
52 cm	2604,5	0,2	144,5	nd	-	nd	397,6	nd	282,4	nd	467,5	nd
56 cm	500,5	0,4	8,9	nd	-	nd	nd	nd	nd	nd	nd	nd
64 cm	2331,1	0,5	103,1	190,7	-	491,9	35,7	nd	233,8	190,7	181,5	nd
72 cm	1135,7	0,5	105,8	15,3	-	14,1	144,7	nd	120,2	nd	227,8	41,3
80 cm	891,9	0,4	28,2	nd	-	nd	74,4	nd	69,5	nd	86,7	nd
88 cm	-		-	-	-	-	-	-	-	-	-	-
96 cm	2206,6	0,5	50,6	nd	-	nd	97,5	nd	nd	nd	149,1	nd
104 cm	425,5	0,4	41,5	nd	-	nd	35,4	nd	37,9	nd	45,6	nd
112 cm	952,6	0,4	44,3	nd	-	nd	47,5	nd	54,3	nd	76,8	nd
120 cm	393,3	0,4	18,1	nd	-	nd	37,3	nd	30,4	nd	39,9	nd
128 cm	464,0	0,4	30,3	nd	-	nd	31,9	nd	44,1	nd	37,9	nd
136 cm	630,3	0,3	32,1	nd	-	nd	63,9	nd	76,7	nd	128,4	nd
144 cm	659,2	0,4	33,5	nd	-	nd	60,0	nd	84,3	nd	72,5	nd
152 cm	961,5	0,2	nd	nd	-	nd	nd	nd	nd	nd	nd	nd
160 cm	693,6	0,3	76,4	nd	-	nd	95,2	nd	71,8	nd	149,5	nd
166 cm	372,8	0,3	426,5	nd	-	nd	nd	nd	nd	nd	297,0	nd